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BRIEF SURVEY OF USSR AIR POLLUTION LITERATURE

Volume XX

CATALYTIC PURIFICATION OF EXHAUST GASES

Edited by

M. Y. Nuttonson

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AMERICAN INSTITUTE OF CROP ECOLOGY

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AMERICAN INSTITUTE OF CROP ECOLOGY
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The report deals with air pollution in large cities and in closed industrial premises, and with the toxicity of automobile exhaust gases under various operating conditions. It also deals with methods of reducing the atmospheric concentration of noxious substances. The particularly favorable prospects of catalytic purification as compared with other forms of purification is noted. Also included is patent data with emphasis on the catalytic oxidation of carbon monoxide, complete oxidation of hydrocarbons, and catalytic reduction of nitrogen oxides as the most common method of removal of nitrogen oxides from gases. The influence of the nature of the catalysts, composition of gaseous mixtures and nature of the toxic components on the conditions of the process is discussed. The results of experimental studies aimed at the development of new oxidation catalysts on supports are discussed. Considerable space in the monograph is devoted to methods of obtaining active, stable, low-percentage catalysts of carbon monoxide oxidation, to the role of the carrier, and to the mechanism of the process.

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PREFACE

The present volume presents a translation of a Russian monograph* intended for the technical staff of scientific research institutes and of industrial laboratories, for members of university faculties, for students specializing in the field of catalysts and gas purification, and for technicians engaged in the automotive transport industry.

The monograph deals with air pollution in large cities and in closed industrial premises, and with the toxicity of automobile exhaust gases under various operating conditions. It also deals with methods of reducing the atmospheric concentration of noxious substances. Emphasis is on the catalytic oxidation of carbon monoxide, the complete oxidation of hydrocarbons, and the removal of nitrogen oxide from gaseous mixtures. There is also a survey of relevant literature. The authors present some observations on new catalysts that were the subject of experimental investigations made at the Institute of the Academy of Sciences of Kazakh SSR. Considerable space in the monograph is devoted to methods of obtaining active, stable, low-percentage catalysts of carbon monoxide oxidation, to the role of the carrier, and to the mechanism of the process.

It is hoped that the monograph selected for presentation in this volume will be conducive to a better appreciation of some of the air pollution investigations conducted in the USSR. As the editor of this volume I wish to thank my co-workers in the Air Pollution Section of the Institute for their valuable assistance.

M. Y. Nuttonson

February 1973

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* "Kataliticheskaya Ochistka Vykhlopnykh Gazov". (Catalytic Purification of Exhaust Gases.) D. V. Sokol'skiy, N. M. Popova. Akademiya Nauk Kazakhskoy SSR. Institut Khimicheskikh Nauk. Izdatel'stvo "Nauka" Kazakhskoy SSR. Alma-Ata, 190 pages, (1970).

INTRODUCTION

The removal of noxious impurities from the atmosphere of large cities, chemical complexes, and closed industrial spaces (shafts, holds, etc.) constitutes at the present time one of the main problems facing mankind. Public health is threatened by discharges from industrial enterprises and exhaust gases of motor transport containing a number of toxic components (carbon monoxide, nitrogen oxides, carcinogenic agents, etc.), whose concentrations in the vicinity of industrial enterprises and heavily traveled streets are many times the sanitary permissible levels. This is particularly harmful for cities with poor natural aeration (Los Angeles, Alma-Ata, and others).

The elevated content of toxic components in exhaust gases seriously complicates the use of diesel-powered equipment in underground mines. Foreign experience in the operation of diesel engines indicates considerable advantages of trackless self-propelled equipment over electric power (the labor productivity increases, the cost of mining of the ore is reduced, etc.).

Because of increased capital investments in the chemical and mining industries and of a considerable expansion of motor transport, the removal of toxic components from exhaust gases constitutes a particularly serious and pressing problem.

The most promising method of purifying exhaust gases in the near future is catalytic oxidation of the toxic substances. A universal catalyst for the purification of exhaust gases is platinum. A platinum-catalyst gas purifier patented by Houdry in the U.S.A. and other countries in the early 1950's has become very popular and is being mass-produced by Oxy-France Co. In the USSR, a platinum catalyst on aluminum oxide has been proposed for the same purposes by the Karpov Physico-chemical Institute.

Because of its scarcity and high cost, platinum catalyst can be used only for purifying the exhaust gases of engines operating underground.

For this reason, in the last 20-25 years, studies aimed at replacing platinum with other metals and oxides have been conducted in the USSR and abroad.

Since 1960, this problem has been given major attention at the Institute of Chemical Sciences of the Kazakh Academy of Sciences (IKhN AN KazSSR). A number of new catalysts for the removal of carbon monoxide, aldehydes, hydrocarbons, and nitrogen oxides from oxygen-containing gaseous mixtures have been proposed and developed. Laboratory, bench and road tests have shown that the maximum removal of carbon monoxide from the exhaust gases of internal combustion gasoline engines is obtained in the presence of a low-percentage palladium catalyst with properties identical to those of platinum.

A supported palladium catalyst whose method of preparation was worked out at the IKhN AN KazSSR, has been recommended for road tests in gas purifiers designed by LANE (Moscow Scientific Research and Experimental Design Laboratory of Exhaust Neutralization and Problems of Automobile and Tractor Power Engineering).

Results of the first stage of efficiency tests showed that palladium-catalyst gas purifiers achieve a high degree of purification of exhaust gases. The overall efficiency of purification of exhaust gases, involving the removal of carbon monoxide, soot, and hydrocarbons, amounts to 50-100% depending on the type of engine and its operating conditions. Palladium catalysts are equal in efficiency to platinum catalysts produced at home and abroad (Oxy-France).

The vigorous development of industrial organic synthesis, and of other industries in the last decade, and the growth of motor transport have added practical interest to the problem of purification of exhaust gases, and the material accumulated in this field needs to be correlated. A survey of work on the catalytic oxidation of carbon monoxide covering the period 1920-1950 is given by M. Katz [162]. Some aspects of the reaction kinetics of extensive oxidation of hydrocarbons are discussed in the monograph of L. Ya. Margolis [170], but this in our view is inadequate when one considers the large number of studies and patent material in this area.

The present book consists of six chapters. The first gives a survey of the literature on the toxicity of exhaust gases and ways of reducing the content of noxious components in the air. The particularly favorable prospects of catalytic purification as compared with other forms of purification of exhaust gases is noted.

The second, third and fourth chapters present an analysis of the literature, including patent data on the catalytic oxidation of carbon monoxide, complete oxidation of hydrocarbons, and catalytic reduction of nitrogen oxides as the most common method of removal of nitrogen oxides from gases. The influence of the nature of the catalysts, composition of gaseous mixtures and nature of the toxic components on the conditions of the process is discussed. Particular emphasis is placed on a review of studies with a practical bent (high space velocities, etc.).

The chapter "Oxidation of Carbon Monoxide over Low-Percentage Supported Catalysts" discusses the results of experimental studies aimed at the development of new oxidation catalysts on supports. The effect of the method of preparation and of the nature of the support on the activity and stability of low-percentage contacts and on the depth of impregnation, mechanical strength, and regeneration is examined. The chief characteristics of low-percentage supported palladium catalysts are listed.

The fifth chapter contains an analysis of government tests of catalysts produced by IKhN AN KazSSR, conducted at LANE (Moscow) and KazNIPIAT (Kazakh Scientific Research and Design Institute of Motor Transport Alma-Ata) under the direction of I. L. Varshavskiy and based on data supplied by these organizations to IKhN AN KazSSR. Data are given on the behavior of the catalysts during the tests and on the change of activity, surface area, strength, phase composition, and particle size composition of the catalysts.

The book utilizes literature and patent materials from 1920 through 1968, including some information from surveys, for example, on the toxicity of exhaust gases (Korenev [5], Demochka [323]), oxidation of carbon monoxide (Katz [162]), and decomposition of nitrogen oxides (Chernyshev, Zanchko [463]).

The chapter "Oxidation of Carbon Monoxide on Low-Percentage Catalysts" describes experimental data obtained by a group at IKhN AN KazSSR: M. B. Syzdykbayeva, G. A. Shchelkina, N. P. Belova, L. M. Novoselova, B. S. Mukanova, L. M. Rozmanova, and I. N. Man'ko, working under our direction.

The following persons participated in the bench and road tests conducted by several organizations [LANE (Moscow),* Institute Giprouglegormash (Karaganda), KazNIPIAT (Alma-Ata), Volgograd Polytechnic Institute], and in the preparation of experimental batches of catalysts: M. B. Syzdykayeva, G. K. Alekseyeva, Ya. A. Dorfman, Yu. V. Pichugov, T. Ye. Dovlichin, B. Daurenbekov, and others. The phase composition, structure, and surface area were determined by L. N. Gudkova, A. Kh. Shalamov, G. Bedel'bayev, G. A. Shchelkina, and I. N. Man'ko.

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*The tests were conducted by the staff of the Gasoline Engine Neutralization Section under the direction of L. S. Zolotarevskiy.

Chapter 1

TOXICITY OF INTERNAL COMBUSTION ENGINE EXHAUSTS AND WAYS OF REDUCING THE CONCENTRATION OF TOXIC COMPONENTS IN THE AIR

Analysis of air on streets and in closed spaces where motor transport is operating shows that in some cases the content of noxious components is many times greater than the sanitary permissible levels. The single maximum permissible concentration of carbon monoxide in atmospheric air is 6 mg/m^3 [48]. According to the data of [4], the average carbon monoxide concentration in the major cities of the USSR amounts to around 20 mg/m^3, which is considerably less than the value for the air of major U.S. cities (up to 90 mg/m^3). The average carbon monoxide content on the main streets of Moscow ranges from 4.3 to 12.9 mg/m^3 [48]. It is determined by the traffic density and width of the streets and may exceed the permissible levels [52].

Analysis of air in the vicinity of traffic flow (up to 2000 automobiles per hour) on certain arterial streets of Volgograd and Chelyabinsk has shown that the concentration of nitrogen oxides and carbon monoxide in the air over the pavement is 2-5 times higher than the permissible value [1, 2].

V. G. Devyatka [3], who studied the pollution of air with carbon monoxide on streets as a function of their traffic load has pointed out that the carbon monoxide content ranges from 0.0004 to 0.21 mg/l, and in the vicinity of the traffic flow it may amount to 1.5-7.1 mg/l.

The chief source of carbon monoxide pollution of air in large cities is the motor transport, foundries of metallurgical plants (up to 10% CO), waste gases of petroleum refineries, chemical complexes such as caprolactam plants (6% CO), coking plants (up to 7% CO), and the like.

It is well known that on heavily traveled streets (2-3 thousand automobiles per hour), the carbon monoxide concentration in some cases is 10 times higher than the maximum permissible sanitary level [7]. For the same traffic density, the carbon monoxide contamination of areas adjacent to a main artery varies widely. In sections with a perimetric layout, angular blocking of houses and small gaps between them, the air is more polluted with automobile exhausts than in sections with regular layouts. According to the data of Kh. B. Berdyyev et al. [8], the average carbon monoxide content in living quarters is highest on the third floor and 6-8 times greater than the maximum permissible levels.

The problem of purifying exhaust gases in closed buildings and confined spaces such as shafts, holds, sea ports, and open-pit mines is most urgent.

According to the data of a sanitary-epidemiological station, the air pollution levels in Alma-Ata in 1966 substantially exceeded the sanitary permissible values.

According to the data of the Kazakh Oncology Institute, areas with major highways (50th October Anniversary Prospect, Abaya Prospect), constitute zones of maximum pollution with 3,4-benzpyrene, a carcinogenic compounds causing lung cancer (up to 0.227 μg/100 m^3) [9].

The accumulation in humid air of toxic components of exhaust gases from motor transport and waste gases from chemical plants and furnace systems has catastrophic effects on the population. Thus, in Belgium in 1930, damage to the respiratory tract and mucous membranes was observed on a mass scale; the death rate during that period was 10.5 times the expected rate under normal conditions. A similar phenomenon was also observed in Pennsylvania in the eastern part of the U.S.A. (Donora) in 1948, in London in 1952, and in the Ruhr region in 1962. Frequent smogs have a harmful effect on the inhabitants of Los Angeles [10]. Frequently, the emission of large quantities of hydrocarbons causes the formation of fogs, particularly in areas with high contents of soot and moisture in the air. For this reason, motor transport is sometimes halted for 10-12 shifts in deep open-pit mines (depth of 200 m or more) [11]. When the natural air exchange is disturbed, the pollution exceeds the permissible sanitary levels, for example, the amount of aldehydes on the bottom of the pit is 30-40 times the allowed level [12].

A high content of toxic components in exhaust gases also seriously hampers the use of diesel-powered equipment in underground mines, although experience with diesel engines in underground operations abroad (U.S.A., France, Canada, Sweden) indicates [13] considerable advantages of trackless self-propelled equipment over electric power (increased labor productivity, decrease of the cost of mining of the ore). It follows from these data that as motor transport, whose use in the national economy and present-day technology is on the increase, gradually expands, the pollution of atmospheric air with exhaust gases grows.

The process of combustion of liquid fuel in engine cylinders involves the formation of combustion products in the form of carbon dioxide, carbon monoxide, water, and other compounds. Tests performed during the last two decades in the Soviet Union and abroad, involving analysis of exhaust gases of gasoline and diesel transport engines by means of the most recent analytical methods, have shown that the composition of the exhaust gases of internal combustion engines includes several dozen components such as hydrogen, carbon dioxide, oxygen, nitrogen, and toxic gases: carbon monoxide, nitrogen oxides, saturated and unsaturated hydrocarbons (methane, ethane, benzene, propane, ethylene, hexane, etc.), aldehydes (acrolein, formaldehyde, acetaldehyde) and soot [14]. The composition of the exhaust of engines operating on sulfur-containing fuel also includes sulfur dioxide.

When an engine runs on ethyl gasoline, oxides and other compounds of lead injurious to the respiratory tract appear in the exhaust. The amount of lead in air is directly proportional to the traffic density and may reach 4-12 mg/m^3, decreasing with the height [15].

The content of toxic substances in the exhaust of diesel and gasoline engines varies and depends on the type of engine and its operating conditions (Table 1), and also on the quality of the fuel, composition of the fuel mixture in the engine cylinders, velocity and conditions of traffic, systems of ignition and fuel feed control, qualifications of the service personnel, etc. As is evident from Table 1, the amount of all the toxic components in the exhaust gases exceeds the maximum permissible levels tens and hundreds of times. The composition of the exhaust gases of gasoline and diesel engines varies considerably. Engines running on gasoline are characterized by a lower oxygen content, a higher content of carbon dioxide and a particularly high content of carbon monoxide. This is one of the chief factors preventing the use of gasoline engines in closed spaces, since aeration of the latter requires 50-100 times more air than in the case of diesel engines.

The complete combustion of fuel in engine cylinders requires a sufficient amount of oxygen. A deficiency of the latter causes a sharp increase in the content of hydrogen and carbon monoxide.

The extreme toxicity of carbon monoxide and its lack of odor and color make this gas particularly dangerous. Its ability to displace oxygen from compounds with hemoglobin is due to the greater affinity of hemoglobin for carbon monoxide (200-300 times greater than for oxygen), so that carboxyhemoglobin is formed [16, 18, 22]. Carbon monoxide damages the nervous and cardiovascular systems [16].

The maximum permissible carbon monoxide concentration in the air of industrial enterprises is 0.0016 vol. % (0.02 mg/l). If the carbon monoxide content of inhaled air is 0.1%, death occurs after 30-60 min, and if 1% or higher, immediately [17]. When nitrogen oxides are present in air. the toxicity of carbon monoxide increases and its allowed content in air should be decreased by a factor of 1.5, since the combined presence of these gases intensifies their effect.

Sulfur dioxide, which is formed in the combustion of sulfur-containing fuel, even when present in low concentrations, produces an unpleasant taste in the mouth and causes irritation of the mucous membranes of the nose, nasopharynx, trachea and bronchi, manifested in coughing spells, hoarseness, etc. A single inhalation of very high sulfur dioxide concentrations causes dyspnea and a rapid impairment of consciousness. Irritation of the mucosa of the eyes and coughing are caused by a concentration of 0.05 mg/l. Man can withstand a sulfur dioxide concentration of 0.3 mg/l for only 1 minute [18].

The maximum permissible sulfur dioxide concentration in the air of industrial enterprises is considered to be 0.02 mg/l [19].

Table 1

Typical Content of Main Components of Exhaust Gases of Internal Combustion Engines

Component	Gasoline Engine	Diesel Engine	Permissible Content in Air, mg/m^3 [48, 78]		Fatal Dose
			Maximum Single	Mean Daily	
Carbon Monoxide	0,5—12,0 Vol. %	0,01—0,50 Vol. %	6,0	1,0	1 об. %
Hydrogen	0,0—5,0	—	—	Dangerously explosive	
Aldehydes	0,0—0,2 mg/l	0,001—0,009 mg/l	0,30**** 0,035	0,1* 0,0005****	0,35 mg/l in the course of 10 min
Nitrogen	74,0—77,0 Vol. %	76,0—78,0 Vol. %			
Hydrocarbons	0,2—3,0 Vol. %	0,009—0,5 Vol. %	5,0*** 3,0**	1,5*** 3,0**	
Nitrogen Oxides (in terms of N_2O_5)	0,0—0,8 Vol. %	0,0002—0,5 Vol. %	0,3	0,1	6 mg/l in the course of 6-8 min
Lead Compounds					0,0007 mg/l
H_2O Vapor	3,0—5,5 Vol. %	0.5—4,0 Vol. %	Nontoxic		
Oxygen	0,3—8,0 Vol. %	2,0—18,0 Vol. %			
Carbon Dioxide	5,0—12,0 Vol. %	1,0—10,0 Vol. %			
Soot	0,0—0,04 g/m^3	0,01—1,1 g/m^3	0,15	0,05	Carcinogenic
3,4-Benzpyrene	10—20 γ/m^3	Up to 10 γ/m^3	Carcinogenic		

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* Given for acrolein, ** propylene, *** gasoline, **** formaldehyde.

Nitrogen oxides are present in the composition of exhaust gases in the form of nitric oxide and nitrogen dioxide. They are formed by the reaction between atmospheric nitrogen and oxygen or water vapor at high pressure (28-35 atm) and a temperature of 540-650° [20] during each compression in the cylinders. The fuel does not participate directly in this reaction.

The literature indicates a direct relationship between the pollution of the atmosphere with nitrogen oxides and the proximity of nitric acid plants [32], and also the number of passing automobiles [12]. Nitrogen oxides are very toxic. In the most typical cases, poisoning with nitrogen oxides begins with a light cough which passes after awhile. At relatively high concentrations, the irritation of the respiratory tract increases: a heavy cough and sometimes headache, vomiting, etc., are observed.

In nitric oxide poisoning, in addition to the general symptoms, dizziness and weakness are also observed, the face is pale, and the blood pressure decreases. A 6-8 min inhalation of air containing approximately 6 mg/l nitric oxide and a 12 min inhalation of 3 mg/l cause death. Poisoning with nitrogen dioxide is characterized by edema of the lungs followed by bronchopneumonia. A fatal concentration is 0.1 mg/l inhaled for 1 hour [22]. The maximum permissible content of nitrogen oxides in the air of industrial enterprises is 0.005 mg/l [18]. In Los Angeles, where 3.5 million automobiles are in use, under certain weather conditions, a photochemical reaction is possible whereby nitrogen oxides form substances which attack the mucosa of the eyes and also plants and even rubber [23]. According to the data of American investigators, the maximum permissible content of nitrogen oxides in the atmosphere is considered to be 0.025% by volume (based on nitrogen dioxide).

In their effect on the human body, nitrogen oxides are the most toxic components of exhaust gases, and their neutralization by catalytic decomposition or reduction assumes a special importance.

As is evident from Table 1, exhaust gases contain a large amount of hydrocarbons whose concentration ranges from 0.2 to 3.0% depending on the operating conditions of the gasoline engine. On some of Moscow's main arteries, among other hydrocarbons, large amounts of pentane (up to 4.5 mg/m^3) and hexane (up to 4.15 mg/m^3) have been observed [26]. At high concentrations, they have a strong narcotic effect. In low concentrations, methane-series hydrocarbons lower the blood pressure. The concentrations of these hydrocarbons in the atmosphere of Moscow were as high as 7-8 mg/m^3 in the summer of 1967 and exceeded the level of their physiological action [25].

The composition of internal combustion engine exhausts includes aldehydes, particularly crotonaldehyde and formaldehyde, whose amounts increase with the load on the engine during starting, acceleration and operation on mountainous terrain. Symptoms of poisoning with formaldehyde vapors include conjunctivitis, head cold, bronchitis, etc. A slight irritant effect on the mucosa of the eyes and respiratory tract was observed in cases where the formaldehyde concentration ranged from 0.001 to 0.0095 mg/l. A 0.025 mg/l concentration of aldehydes causes an acute irritation of the mucosa of the eyes. A 10 min stay in an atmosphere containing acrolein in 0.35 mg/l concentration is fatal to man. The maximum permissible concentration is 0.001 mg/l.

Carbon dioxide present in a concentration up to 0.4% in air stimulates breathing, and above 4% causes irritation of the respiratory tract, tinnitus, dizziness, and headache.

Soot, whose content in the exhaust of diesel engines is high, constitutes a major peril in air pollution. It consists mainly of carbon particles. Its elementary analysis gives the following breakdown: 90-95% carbon, and 5-10% balance divided equally between hydrogen and oxygen [26]. Soot has a large adsorptive capacity for highly condensed hydrocarbons including 3,4-benzpyrene, a carcinogenic substance causing cancerous diseases.

Motor transport exhausts and petrochemical plants [28] constitute the two major sources of contamination of the atmosphere with 3,4-benzpyrene. It has been established [29] that the soot on the inner walls of exhaust pipes of carburetor engines contains a larger amount of 3,4-benzpyrene than the soot of diesel engines (200 γ per g of soot of a gasoline engine, versus 1 γ per g of soot of a diesel engine).

Contamination of the atmosphere with 3,4-benzpyrene in major cities increases in direct proportion to the number of inhabitants. In cities of the Soviet Union, the concentration of 3,4-benzpyrene in air is approximately 10 times less than in England and the U.S.A. [30].

The book of L. M. Shabad and P. P. Dikun [30] notes the relationship between the pollution of the atmosphere with 3,4-benzpyrene in major cities and the increasing incidence of lung cancer.

Of considerable interest is the effect of the operating conditions of an engine on the composition of the exhausts. In this sense, there is a marked difference between the combustion of fuel in a carburetor gasoline engine and its combustion in a diesel engine. However, in both cases the formation of incomplete combustion products is due to a deficiency of the oxygen required for the complete combustion of the fuel, i.e., the quantity of these products increases as the air-fuel ratio is decreased.

The operating characteristics of diesel engines are such that as the load decreases, the composition of the fuel mixture becomes leaner, and therefore the content of the toxic components decreases at small loads on the engine. Whereas during idling the carbon monoxide content amounts to hundredths of one percent (vol. %), at maximum loads it reaches its maximum, i.e., 0.5%. This also applies to the content of aldehydes and hydrocarbons.

One American study [31] cites data on the variation in the concentration of noxious impurities in the composition of exhaust gases of diesel engines. The content of nitrogen oxides is maximum during acceleration (0.085%) and normal running (0.025%). and that of carbon monoxide, during acceleration (up to 0.1%).

In diesel engines, the composition of exhaust gases depends on the mode of injection of the fuel into the engine cylinder. Straight injection is better than lateral, but is associated with the formation of large amounts of nitrogen oxides. The composition of exhaust gases of diesel engines with different degrees of wear, cited in [32], shows that the exhaust contains from 2.1 to 3.3% of unburned fuel (this causes the formation of soot on the surface of catalysts during catalytic purification). The amount of soot and oil increases particularly in worn diesel engines, which run on richer mixtures (air: fuel = 27:1) than new engines (air: fuel = 40:1). In the exhaust of worn engines, the content of aldehydes and volatile fatty acids is 3-10 times greater. The amount of soot in the exhaust of diesel engines decreases when barium and other fuel additives that improve the combustion processes are used [33].

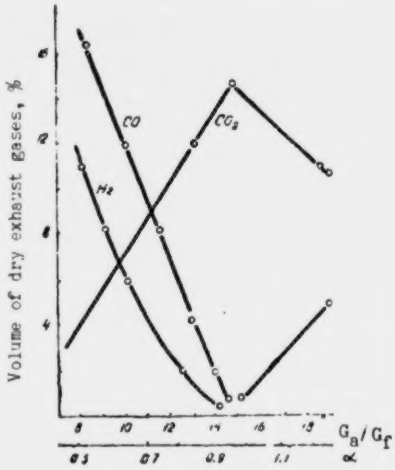

Fig. 1. Content of carbon monoxide, hydrogen, and carbon dioxide in the exhaust of a carburetor engine vs. excess air coefficient [323].

The paper of S. S. Filatov [12] compares the compositions of exhaust gases from different makes of diesel dump trucks. It shows that the lowest concentrations of toxic components (carbon monoxide 0.05%, nitrogen oxides 0.0029%, aldehydes 0.002%) are observed in the exhaust of the most advanced four-stroke engine of the MAZ-525 truck.

The condition of the fuel system of diesel engines is very important. Thus, it is shown in [63] that the replacement of injectors in the YaAZ-210 Ye diesel engine caused a severalfold decrease in the content of aldehydes in the exhaust gas.

The composition of gasoline engine exhausts is chiefly determined by the air-fuel ratio in the working mixture at the instant of ignition. In operation with an excess air coefficient $\alpha<1$ (0.7), the contents of hydrogen and carbon monoxide may reach considerable values because of incomplete combustion, and only at $\alpha>1$ (1.01-1.1) does it approach zero (Fig. 1) [323]. O. K. Demochka notes that under urban conditions, the engine of the GAZ-51 motor vehicle runs mainly on a fuel mixture with α = 0.6-0.95, which decreases to 0.5-0.7 during idling and deep throttle conditions, substantially increasing the carbon monoxide content in the exhaust.

Data on the composition of the exhaust gas of gasoline engines as a function of the content of fuel vapor in the air-fuel mixture are given by M. S. Gershenovich and N. Z. Kotelkov [6]. The lowest content of toxic components and hydrogen in the exhaust gas is observed when engines operate on lean mixtures.

The effect of the air-fuel ratio on the hydrocarbon content is similar [14, 20, 35], as indicated by the data of Fig. 2.

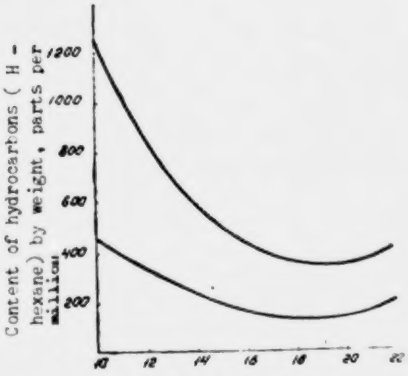

Fig. 2. Change in the content of hydrocarbons in the exhaust as a function of the mixture ratio [14].

The amount of toxic components in the exhaust gases of gasoline engines varies with the run of the engine, its load, power, and operating conditions. Figures 3 and 4 show the content of the various components of exhaust gases as a function of the traveling speed of the automobile and its loads [14].

It is evident that a considerable content of products of incomplete fuel combustion - carbon monoxide and hydrocarbons - is observed under conditions close to idling and during idling, when because of the combustion of an enriched fuel mixture, the amount of carbon monoxide amounts to 5%, and also at higher traveling speeds of the automobile.

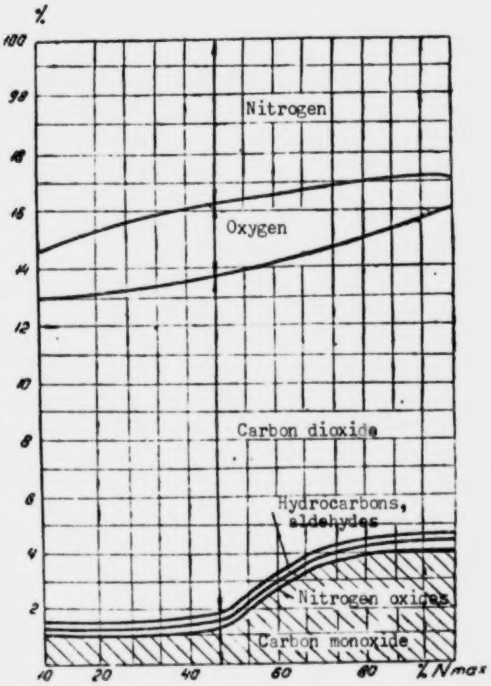

Fig. 3. Change in the relative amounts of gasoline engine exhaust components as a function of the load [14] .

At a speed of 120 km/hr, the carbon monoxide concentration rises to 6% of the total gas volume. At the same time, in the range up to 50% load at a speed of 60-70 km/hr, the content of incomplete combustion products declines sharply, and in some cases none can be detected at all. The same applies to nitrogen oxides and hydrocarbons. At a load of up to 20-50% on the engine, their content is very low, but increases sharply at maximum power. As the load of the gasoline engine increases, the carbon monoxide content can, as is evident from Fig. 3, rise from 1 to 4-5 vol. %.

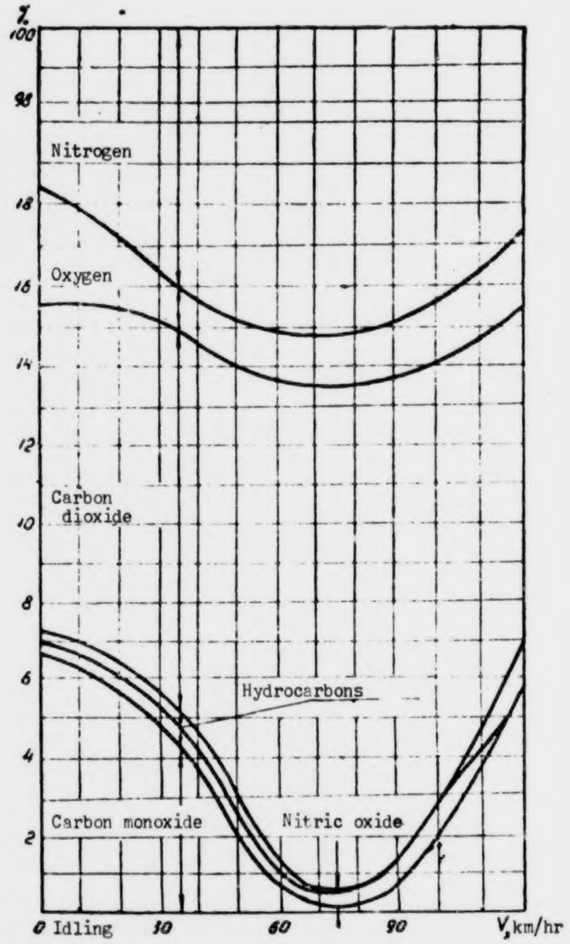

Fig. 4. Composition of dry exhaust gases vs. traveling speed of automobile with "Moskvich-408" engine traveling along a horizontal hard-surface road [14].

The relative duration of the running of trucks under forced idling (braking) and independent idling (stopping of buses during discharging in wintertime) conditions, when they operate on enriched mixtures, amounts to 18 and 30% respectively of the total time of operation [36]. It is this mode of operation of automobiles in cities that is primarily responsible for air pollution [323].

In engine braking, the fuel in the cylinders burns at $\alpha = 0.67-0.68$; the ignition and combustion of such a mixture are difficult. As a result, part of the fuel does not participate in the combustion and is discharged in the form of spray particles, and the gases contain considerable carbon monoxide and unsaturated hydrocarbons. A large amount of the fuel burns incompletely, up to 4-6% under forced idling conditions of the CAZ-51 motor vehicle and up to 8-14% on mountainous terrain [37].

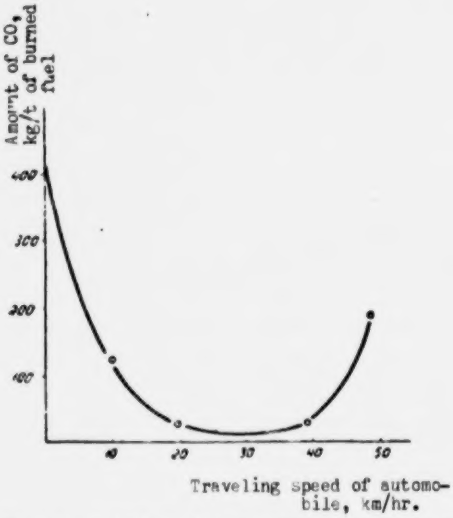

Fig. 5. Emission of carbon monoxide in the exhaust gas under different conditions of operation of ZIL-150 motor vehicle [5].

In order to decrease the content of toxic components in the exhaust gases of carburetor engines under three types of running conditions, a vacuum regulator is recommended which permits the admission of extra air into the combustion chambers [36]. When this regulator is used, one can achieve an 80-90% reduction in carbon monoxide concentration and a 10-fold reduction of the content of formaldehyde and other substances (acrolein, benzene).

An interesting calculation is given in M. S. Korenev's survey [5] of the possible emission of carbon monoxide for different operating conditions of the ZIL-150 motor vehicle (Fig. 5). It is evident that about 30 kg of carbon monoxide is evolved by the combustion of 1 ton of gasoline in the engine, at a traveling speed of 20-40 km/hr. The amount of CO increases at a higher traveling speed and during idling. These data are somewhat relative, but they can give an idea of the amounts of emitted carbon monoxide when it is necessary to have a general estimate of the toxicity of the traffic.

In our view, a more correct method of evaluating the toxicity of exhaust gases has been proposed by I. L. Varshavskiy, L. S. Zolotarevskiy and L. Ye. Ignatovich [38]. They refer the amount of emitted carbon monoxide in grams to a unit of the path traveled by the automobile (Fig. 6).

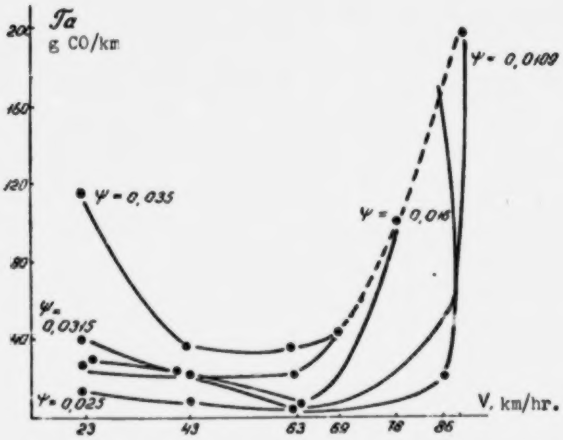

Fig. 6. CO toxicity characteristic of ZIL-150 motor vehicle after bench test data [38].

Calculation of the "specific toxicity" values (determined by the volume of air necessary for neutralizing the individual toxic components of an exhaust gas), carried out by L. S. Zolotarevskiy, made it possible to determine the danger contributed by each of the toxic substances. When gasoline engines operate on lean mixtures, the main toxic components are products of incomplete fuel combustion: carbon monoxide (up to 95% of the total toxicity) and soot in the case of a diesel engine. In operation on rich mixtures (gasoline engine), and as the load on the diesel engine increases, the chief danger is due to nitrogen oxides, whose toxicity contribution climbs to 55-85% [14].

According to the data of Fitten [31], the content of toxic components under different conditions of motion may fluctuate considerably: carbon monoxide from 1.8 to 7.0%, hydrocarbons from 0.1 to 1.0, nitrogen oxides from 0.002 to 0.105%, aldehydes from 0.001 to 0.03%.

Table 2

Carbon Monoxide Content of Exhaust Gases (ZIL-120) in Percent by Volume [20].

Traveling Speed of Automobile, km/hr	For Normal Technical Condition of Engine		For Worn Engine
	With Properly Adjusted Carburetor	With Carburetors Giving a 25% Overfeed	
0	1,5	3,5	6,6
10	1,5	3,0	—
15	—	—	6,2
20	0,2	1,3	6,1
30	0,2	1,7	3,4
40	0,2	—	2,3
50	1,2	—	—

Data obtained by the author of [31] in a study of the operation of 22 automobiles indicate an increasing amount of CO and hydrocarbons during idling and of nitrogen oxides in normal operation and during acceleration, and also an increase in the amount of aldehydes during deceleration.

Among the many factors affecting the composition of the exhaust gases are the structural characteristics of the engines, the extent of their wear, and their technical condition (carburetor adjustment, etc.). Thus, N. Z. Bitkolov [20] has shown that the exhaust of a four-stroke engine contains a considerably smaller amount of toxic components than that of two-stroke engines. Furthermore, the volume of exhaust gases formed by the combustion of 1 kg of fuel in a four-stroke engine decreases markedly because of the absence of forced air supercharging.

Obstruction and malfunctions of air filters and a prolonged operation of the engine cause a malfunction of the fuel- and air-feed equipment and a decrease of the adjusted air-fuel ratio. Owing to the operation on enriched mixtures, the composition of the exhaust gases of improperly adjusted and worn engines contains larger amounts of carbon monoxide and hydrocarbons than do the exhaust gases of new engines. For example, the carbon monoxide content in the exhaust gases of a worn ZIL-120 engine is four times greater than in the exhaust of a new engine (Table 2).

According to the data of Zh. G. Manusadzhyants and L. L. Stepanov [39], in 70% of 368 operating GAZ-51 and ZIL-164 motor vehicles that were studied, the idling system of the carburetor was found to be faulty, and in 50% an improper adjustment of the proportioning system was observed. As a result, the exhaust gases of most automobiles contained from 6 to 13% carbon monoxide. After the fuel feed process was adjusted, the amount of carbon monoxide decreased sharply (to 1%). The grade of fuel has a considerable effect on the carbon monoxide content. Data on this effect are listed in Tables 3 and 4.

Table 3

Carbon Monoxide Content of Exhaust Gases as a Function of Gasoline Grade Used During Operation of ZIL-120 Engine.

Speed, km/hr	CO Content, %	
	A-70 Gasoline	A-56 Gasoline
0	**1,5**	**3,5**
10	**2,5**	**3,1**
20	**1,5**	**3,0**
30	**1,5**	**3,0**
40	**1,5**	**1,5**

Table 4

Content of Carbon Monoxide and Hydrocarbons in the Exhaust of ZIL-156 Engine During Idling [48].

Distance of Sample Collector from End of Exhaust Pipe, cm	Gasoline		Compressed Gas	
	Content, mg/m^3			
	Carbon Monoxide	Hydro-Carbons	Carbon Monoxide	Hydro-Carbons
10	**279,3**	**1044,2**	**71,5**	**7,3**
	478,8	**991,1**	**53,0**	**7,46**
	118,7	**151,4**	**11,0**	**3,83**
200	**106,4**	**79,8**	**17,0**	**4,75**

As is evident from the tables, the use of gaseous and high-octane fuel without tetraethyllead additives substantially decreases the carbon monoxide and hydrocarbon contents of the exhaust gases.*

The decrease of atmospheric pressure associated with the operation of engines in mountainous areas affects the air-fuel ratio. In automobiles with a normally adjusted carburetor ($\alpha = 1.0-1.1$), when the air pressure is reduced [40] by 10% as compared with normal pressure for which the feed has been adjusted, the fuel consumption increases by 7%. When the pressure drops 30%, which corresponds to the pressure at 3000 m above sea level, the specific fuel consumption increases by 30%. The decrease of the excess air coefficient causes a sharp increase in the carbon monoxide concentration of the exhaust gases.

The same effect is observed when the pressure of the air entering the engine is reduced by passing the air through the throttle valve in a worn engine.

Tests performed by N. Z. Bitkolov [20] on two engines at pressures of 756, 660, and 610 mm Hg also showed that as the air pressure decreases, the carbon monoxide content of the exhaust gases increases markedly, and the air-fuel ratio decreases.

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* Results of Tables 2, 3 and 4, based on unpublished data of a series of studies, were obtained under incomparable conditions and must be considered debatable.

Interesting relationships were found by L. M. Shabad and A. Ya. Khesina [27] in the effect of the operating conditions of the engine on the content of carcinogenic hydrocarbons, particularly 3,4-benzpyrene in the exhaust of gasoline and diesel engines. In the operation of the YaAZ-204 engine, the amount of 3,4-benzpyrene increases from 4.3 μg/min at a load of 10% of maximum power to 20.1 μg/min at maximum power. During idling, the amount of 3,4-benzpyrene increases from 1.3 μg/min when the engine operates at 500 rpm to 8.41 μg/min at 1500 rpm. A similar pattern was observed in other brands of diesel engines. Thus, in [53], where the content of 3,4-benzpyrene was studied in the exhaust gas of a two-stroke three-cylinder engine, an increase of its concentrations was shown during idling and at a traveling speed of 30 km/hr.

The largest amounts of 3,4-benzpyrene are discharged during incomplete combustion of the fuel resulting from an increased fuel feed, especially when the engines are started up or turned off, when the automobile starts to move, and at intersections.

For a carburetor engine, the content 3,4-benzpyrene increases at high loads, in idling (particularly at low rpm), and when low-octane gasoline is used. The content of 3,4-benzpyrene in automobiles operating on overrich mixtures increases sharply (by a factor of two) [55].

The content of carcinogens in exhaust gases can be cut in half by decomposing them catalytically [181, 27] in gas purifiers with a Pt and copper oxide-chromium oxide catalysts, and also by using a special anti-smoking additives (1%) to the diesel fuel which decrease the amount of 3,4-benzpyrene by 60-80% [41].

State road tests of catalytic gas purifiers on flat terrain in Moscow and in Alma-Ata, located at an altitude of 800-1000 m above sea level, conducted by LANE and KazNIPIAT, yielded some interesting data on the change of the composition of exhaust gases from various engines.

Figures 7 and 8 show data on the average oxygen content of exhaust gases of different engines in the areas of Moscow and Alma-Ata (processed data of LANE and KazNIPIAT, obtained by analyzing the gases of three automobiles of each brand with gas samples taken once and twice).

It is evident from Fig. 7 that the maximum quantity of oxygen is present in the gas when the automobiles are idling, and as the traveling speed increases, this quantity decreases, then increases slightly at 60 km/hr. The average oxygen content in the exhaust during idling ranges from 5 to 15%, reaching a maximum for GAZ-51, ZIL-130 (12-15%) and a minimum for "Moskvich" motor vehicles, 5-6%.

During the operation of different motor vehicles, in Alma-Ata, the average oxygen content in the exhaust decreased to 5-7% during idling and ranged from 3 to 5% at 30 km/hr and from 3 to 6% at 60 km/hr.

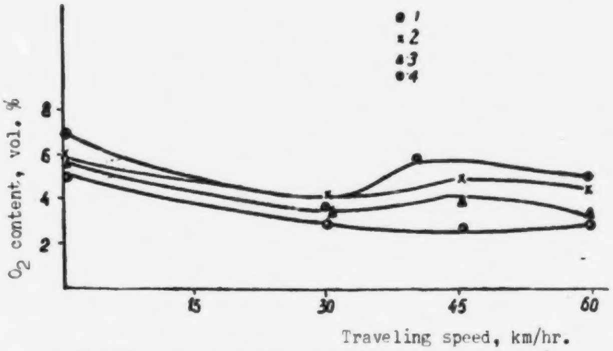

Fig. 7. Oxygen content of exhaust gases of various engines operating in the Moscow area as a function of the traveling speed.

1 - ZIL-585; 2 - GAZ-51; 3 - ZIL-130; 4 - "Volga"; 5 - "Moskvich-408".

The carbon monoxide content of exhaust gases of the engines operated in Moscow ranged from 0 to 10% during idling depending on the brand of the motor vehicle; it decreased to 2-3% for "Moskvich" and to 0-6% for "Volga", ZIL-585, and GAZ-51 as the traveling speed increased to 60-75 km/hr. The minimum amount of carbon monoxide during idling was observed in the exhaust of ZIL-130 (up to 2.0-3.0%), and the maximum in the case of "Volga" and "Moskvich" (0-4%, 3.7-10.0%). The CO_2 concentration in the exhaust of the engines of GAZ-51 and "Moskvich-408" in Alma-Ata considerably exceeded that of the other engines in the Moscow area at speeds of 30-60 km/hr. Whereas in Moscow the carbon monoxide content in the exhaust of the "Moskvich" motor vehicle did not exceed 3-4% in this speed range, in Alma-Ata it ranged from 2 to 10%, and for the engine of GAZ-51 amounted to 0-8% in Alma-Ata and 4-6% in Moscow under all operating conditions. The lowest carbon monoxide content was found in the case of the structurally newer engine PAZ-652 under all operating conditions.

As was shown by the analyses, in addition to carbon monoxide, the composition of the exhaust gases from the engine of GAZ-51 contains a large amount of hydrogen. Its content in the exhaust of some automobiles amounts to as much as 5-6 or more volume percent.

It follows from the analysis carried out by KazNIPIAT on the exhaust gases of 50 automobiles that the carbon monoxide concentration in the exhaust gas of the GAZ-52 engine is related to the hydrogen content.

An arbitrary classification of the motor vehicles into two groups, in the first of which the hydrogen content of the exhaust did not exceed 2.5% (12 automobiles) and in the second was higher than 2.5% (38 motor vehicles),

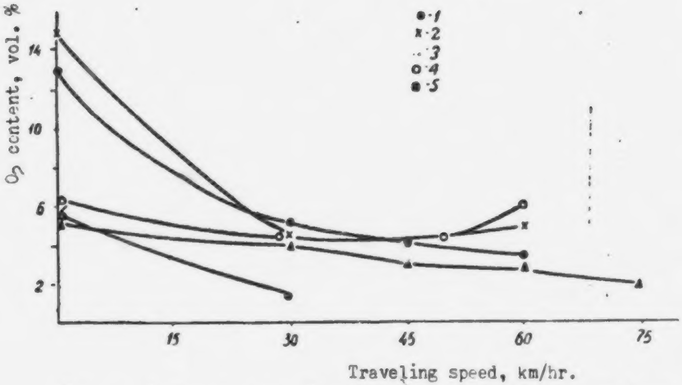

Fig. 8. Oxygen content of exhaust gases of different engines in the Alma-Ata area vs. traveling speed.
1 - GAZ-52; 2 - "Moskvich 408"; 3 - ZIL-585; 4 - PAZ-652.

indicates that these groups are characterized by different limits of fluctuations in carbon monoxide content. In the exhaust gas of motor vehicles of the first group (Fig. 9 a), this content ranges from 0 to 5% under all operating conditions, and in the second group (Fig. 9 b), from 0 to 10-11% at 40 and 60 km/hr and from 5 to 11% during idling. Apparently, the presence of substantial amounts of carbon monoxide and hydrogen in the exhaust gases of most motor vehicles is due to a partial cracking of the fuel and the incompleteness of its combustion caused by an insufficiency of air in the composition of the combustible mixture. This is due to an insufficient adjustment of engines which had been little worn in (most of the motor vehicles had a low mileage), and to the lower atmospheric pressure in Alma-Ata.

Thus, analysis of the literature data indicates that the content of toxic components, especially carbon monoxide, in the exhaust gases of gasoline and diesel engines depends on many factors and shows a particular increase during idling and at high traveling speeds, when increasing the load and braking, stopping and starting, and also in motor vehicles with a maladjusted fuel feed in the case of a worn engine and when the latter operates on low-octane gasoline or when the oxygen content of the air is low (mountainous areas and high mountains).

A substantial reduction in the air pollution of large cities, shafts, open-pit mines, and closed industrial buildings can be achieved by carrying through extensive organizational and technical measures [154].

It is very important to establish more rigid norms for the content of toxic components in engine exhausts and to follow them, particularly in areas where motor transport is the chief source of atmospheric contamination.

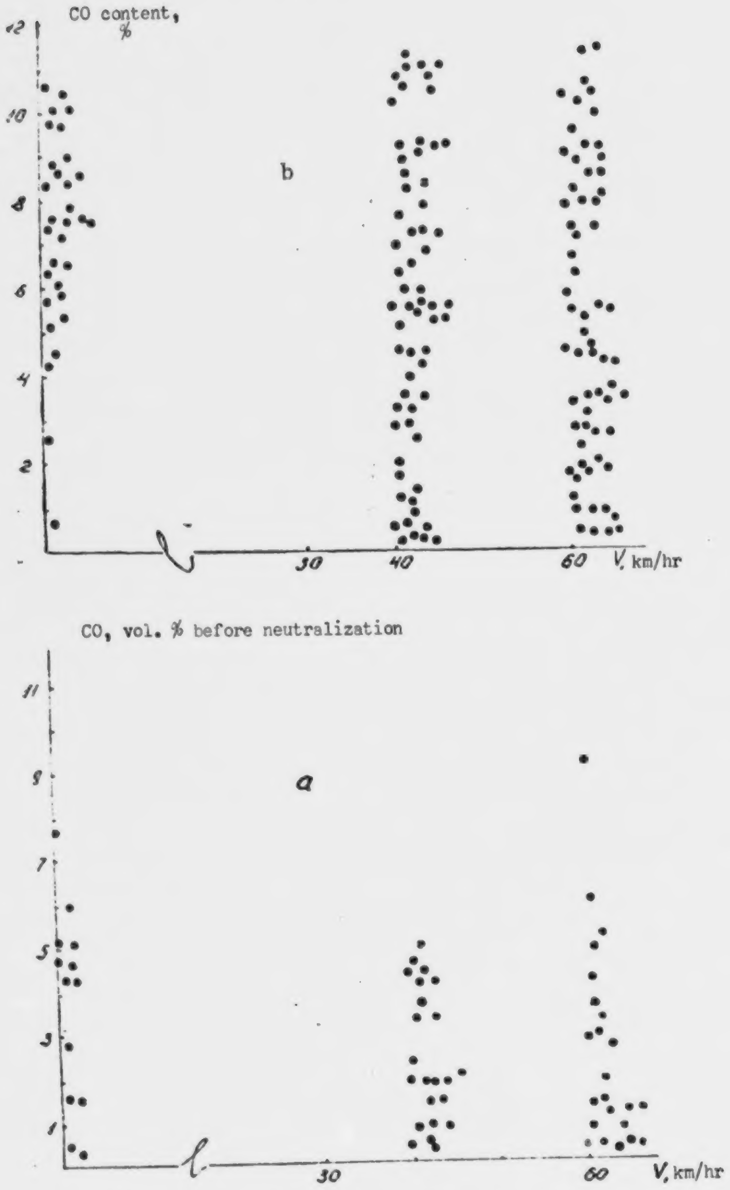

Fig. 9. Range of variation of carbon monoxide content in the exhaust of GAZ-51 automobiles with different H_2 concentrations in the exhaust:
a - H_2 content from 0 to 2.5%; b - from 2.5 to 5.6%.

At present time, the legislatures of many countries (certain states in the U.S.A., England, the German Federal Republic [42]) have imposed restrictions mainly on smoke discharges. For example, the city of Los Angeles prohibits the discharge of smoke with a density of 2 or more units on the Runkelmans scale for more than 3 minutes per hour.

In some countries and states of the U.S.A., where the traffic is particularly congested, the exhaust gases comprise the bulk of the atmospheric pollutants (for example, in Los Angeles, 80% of the total pollution of the atmosphere with hydrocarbons and 65% of pollution with nitrogen oxides are due to motor transport), and restrictions are placed on the concentrations of a number of the components of the exhaust gases. Thus, the laws of the state of California (which apply to the first 80,000 km of the motor vehicle) set the limiting concentrations of toxic components according to the type of engine and its power. For engines with a displacement of 0.2-1.64 l, the carbon monoxide content of the exhaust gas must not exceed 2.3%, and the hydrocarbon content must not be more than 410 parts per million. As the engine displacement increases to 1.64-2.39 l and above, the amount of carbon monoxide must not exceed 1.5-2.0%, and that of hydrocarbons, 275-350 parts per million [34, 143].

In the USSR, the norm recommended for the carbon monoxide content of exhaust gases is 2% of the total volume of these gases. To reduce the pollution of the atmosphere with toxic components of exhaust gases in major cities of the USSR, motor vehicles are converted to high-octane and gas fuel. Thus, in Moscow, 3000 motor vehicles were running on liquefied gas in 1965 [44, 45], continuously moving traffic with a minimum number of intersections is being established, and central arteries are kept free of automotive trucks, particularly those with diesel engines. The construction of underpasses also sharply reduces the carbon monoxide concentration of air [48]. Thus, whereas on Mayakovskiy Plaza in Moscow before the underpass was built the maximum carbon monoxide concentration was 70 mg/m^3 (10 times the permissible level), and the average was 20.7 mg/m^3 (3 times greater), now the maximum value is 15.4 and the average is 8.2 mg/m^3; the hydrocarbon content of air was reduced severalfold.

Among the technical measures aimed at reducing the content of toxic components in the exhaust gases, one must mention first and foremost those taken toward a rigorous observance of the rules of operation and technical servicing of engines (carburetor adjustment, prohibition of the operation of defective engines) and the improvement of the fuel combustion process: introduction of antechamber flame ignition, a special vacuum regulator, and anti-smoking fuel additives [41, 46, 44, 7]. A radical means of decreasing the toxicity of engine exhausts and completely eliminating this problem would be the conversion to electric cars operating on storage and fuel batteries [7, 49].

Among the possible steps toward reducing the toxicity of the exhaust gases of chemical plants and internal combustion engines, major importance is now being assumed by their purification and neutralization by different methods: chemical binding of aldehydes and nitrogen oxides by passing them through liquid filters in the form of scrubbers filled with a solution of sodium sulfate and hydroquinone, sodium carbonate, and catalytic oxidation of the toxic components in the gas phase.

Liquid "neutralizers" permit the binding of 60% of nitrogen oxides and 90% of aldehydes, but do not remove carbon monoxide. The latter can be oxidized in the liquid phase at low space velocities (3×10^3 hr^{-1}) by using a low temperature (20-40°C) homogeneous catalyst consisting of a mixture of complex salts of palladium and copper [50, 51].

Because of the low efficiency of noncatalytic liquid neutralizers with respect to carbon monoxide, they cannot be used for purifying the exhaust gases of gasoline engines and are chiefly employed in diesel engines operating underground. A drawback of this type of gas purifiers is also their size and the frequent replacement of the absorbing solution (once every shift).

The most promising method of purifying exhaust gases containing products of incomplete fuel combustion is the catalytic oxidation of toxic components.

Studies aimed at the development of exhaust-purifying catalysts were carried out in the 1950's in the U.S.A. (Houdry) and in the 1960's in the USSR chiefly by the Institutes NIOGAZ (Central Scientific Research Laboratory for the Purification of Industrial Gases), NAMI (State All-Union "Order of Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute), and later by the Karpov Physicochemical Institute (Moscow), the Institute of Chemical Sciences of the Kazakh Academy of Sciences (Alma-Ata), and by the Azizbekov Institute of Petroleum Chemistry (Baku).

The most universal exhaust-purifying catalyst was found to be platinum. A catalytic gas purifier with platinum deposited in a special manner on ceramic material was patented as a catalyst by Houdry in the U.S.A. This purifier was then adopted widely, for example, introduced into mass production by the "Oxy-France" Co. in France.

It must be noted that the idea of using platinum as a catalyst for purifying exhaust gases was not new. Back in 1938, M. S. Gershenovich and N. Z. Kotelkov proposed for this purpose platinized nichrome consisting of a screen of nichrome steel (d = 0.8 mm) on which platinum was deposited by brazing. The device for gas purification consisted of a cylinder 25.5 cm in diameter and 60 cm long in which 20 screens of platinum nichrome were mounted perpendicular to the cylinder axis.

In the USSR, a platinum catalyst on γ-Al_2O_3 was developed for these purposes: its bench and road tests showed a high efficiency and stability in the purification of diesel and gasoline engine exhausts.

Because of its scarcity and high cost, platinum catalyst can be used only for purifying the exhaust gases of engines operating underground. This has led in the last 20-25 years to many attempts to replace platinum by other metals and their oxides in the USSR and other countries. The research was aimed primarily at selecting the catalysts and studying the kinetics and mechanism of oxidation of the chief toxic components: carbon monoxide, hydrocarbons, and aldehydes. The difficulty of selecting catalysts for purifying exhaust gases lies in the rigid requirements for the specific conditions of their subsequent operation in automobiles: a high efficiency, stability and operational durability at considerable space velocities of the gas flows (up to 100 x 10^3 hr^{-1}), an abrupt change in the catalyst temperature (200-800°), high concentrations of toxic components, and the presence of catalytic poisons (lead, sulfur, soot). A major importance is assumed by the method of preparation of catalysts with a high operational impact strength and wear resistance during the exothermic oxidation processes.

Because of the unusual conditions of operation of exhaust-purifying catalysts, few catalysts are known at the present time (palladium, vanadium) which do not contain platinum and have successfully passed the stage of bench and road tests and provide a high degree of purification of exhaust gases. In spite of intensive research, with the exception of France, no mass production of catalytic gas purifiers for mass-produced automobiles has been set up in any country thus far.

At the Institute of Chemical Sciences of the Kazakh Academy of Sciences, studies on the selection and perfection of exhaust-purifying catalysts have been conducted since 1960. A large amount of experimental material has thus accumulated which has been published in part in the form of individual papers and author's certificates [54, 56-62, 266, 267].

After bench and experimental and road checks (at LANE) one of the proposed catalysts (palladium) has been recommended for mass road tests, the first stage of which - efficiency tests - was carried out jointly by LANE and KazNIPIAT in 1967. The results of the efficiency tests of palladium catalysts under road conditions are presented in Chapter 6 of this book. In the near future, LANE will carry out the second stage of stability and durability tests.

Chapter 2

CATALYTIC OXIDATION OF CARBON MONOXIDE

The catalytic oxidation of carbon monoxide has been extensively studied for the purpose of investigating the mechanism of the process and using different contacts for removing carbon monoxide from air. An exhaustive survey of studies in this area for up to 1950 was given by M. Katz [162]. A practical result of these studies was the development and improvement of "hopcalite," a catalyst successfully used for removing carbon monoxide from air at low temperatures in modern gas masks [21, 165-169, 470].

In the last decade, the rapid development of industrial organic synthesis and the growth of motor transport have created the problem of purification of the exhaust gases of internal combustion engines and waste gases of chemical plants (cracking, caprolactam, rubber, coking, paint and varnish plants, etc.) through removal of toxic components, the bulk of which consists of carbon monoxide, nitrogen oxides, and hydrocarbons. As a result, research on complete catalytic oxidation has assumed an even greater practical importance. In the 1950's-60's, thorough investigations were undertaken to determine the mechanism of the processes and action of catalysts, and their results are being applied in industry.

Table 5 summarizes the literature data on the catalytic oxidation of carbon monoxide. Included are studies where carbon monoxide was oxidized in laboratory units at relatively high space velocities and temperatures approximating the conditions of their subsequent practical application and the removal of carbon monoxide from actually occurring gaseous mixtures.

It is well known that the principal catalysts for oxidation processes (oxidation of SO_2 to SO_3, of ammonia to nitric acid, etc.) are metals, alloys, and oxides (on carriers or in the form of mixtures) of elements of group 8 and other groups of the periodic system.

As is evident from Table 5, in the case of oxidation of carbon monoxide, the researchers' attention was directed to the study of metal and mixed catalysts on carriers. The platinum catalyst in the reaction of carbon monoxide oxidation was studied by N. Z. Kotelkov [6], L. Ya. Margolis, O. M. Todes [97, 374], Houdry [82, 83], Kennan and welling [87], and D. V. Sokol'skiy et al. [54]. Results of bench tests of platinum catalyst in the USSR are described in the papers of V. V. Goncharov and R. V. Malov [70]. Platinum on a metal carrier - nichrome - for the removal of carbon monoxide from gasoline engine exhausts was first proposed by N. Z. Kotelkov back in 1938 [6]. Later, this contact was used for the quantitative analysis of gas mixtures. Judging from the patent literature and statements in the press [82, 83], extensive research on the selection of catalysts for the complete oxidation of toxic components of exhaust gases was carried out by the American Scientist

Table 5.

Catalytic Oxidation of Carbon Monoxide (Laboratory Data).

Catalyst composition	Composition of gas mixture	Space velocity x 10^3 hr^{-1}
1	2	3
Pt/Al_2O_3 on ceramic	Exhaust gas of gasoline engine	90—100,0
Pt/asbestos 0,05—0,1% Pt	1% CO in air	—
Pt/Al_2O_3	Exhaust gas of gasoline engine	80—120,0
Pt/SiO_2	Close to exhaust composition	9,0
Pt/nichrome	Exhaust gas of gasoline engine	3 l/sec, surface of spiral 1.1 m^2
Pt/Al_2O_3	1% CO + air	
AP-56 platinum, freshly prepared	•	•
AP-56 platinum, used	•	•
Pd/chamotte	$CO:H_2=1,76:1$ $CO+H_2=6,3\%$ $\Sigma CO+H_2/O_2=$ [illegible]	10—18
Pd/Al_2O_3	1% CO + air	6—30
Pd/Al_2O_3	•	36—72
$Pt-Pd/Al_2O_3$	•	•
$Pd-Ru/Al_2O_3$	•	•
$Pd-Ag/Al_2O_3$ POI P	•	•
Copper-chromium oxide	$2\% CO+3\% O_2+N_2$	9,5—52
Copper-chromium $CuO:Cr_2O_3=1:2$	1% CO + air	36—72
Copper-chromium GIPKh-105	•	•
Fe_2O_3/Al_2O_3	4% CO in air	6—8
Fe_2O_3/commercial Al_2O_3, promoted with CuO	1—6% CO, O_2 9—19% CO_2, 1-3%, 1—3% CO (regeneration gases)	4—8
CuO/Al_2O_3 (13 6—50 wt. % CuO)	1% CO in air	40
CuO/Al_2O_3 (1:1)	1000—100 parts per million in air	10—16
	Exhaust gas with 1.5—7.0% CO	•
$\frac{CuO/Fe_2O_3}{clay}$	1% CO in air	36—72
$MnFe_2O_4$	2,0—6% CO in air	2,4—6,0
$\frac{CuO/MnO_2}{chamotte}$	$CO:H_2=1,76:1$ $CO+H_2=6,3\%$ $CO+H_2:O_2=1:3$	10—18
$CuMn_2O_4$	2—6% CO in air	2—4

Continuation of Table 5

Degree of oxidation of CO, %						Characteristics of the process	Reference
150°	200°	250°	300°	400°	500°		
4	5	6	7	8	9	10	11
—	—	—	100	100	100	—	[82,83]
8	30	—	73	82	—	—	[97]
—	20	50	100	100	100	—	[70]
—	—	—	100	100	100	—	[87]
—	—	100	100	100	100	—	[6]
—	80—100	100	100	100	100	—	[54]
95	100	100	100	100	100	—	—
65	100	100	100	100	100	—	—
—	—	—	75	—	70—90	—	[86]
—	100	100	100	100	100	—	[85]
—	80—90	100	100	100	100	—	[54]
40	40—75	100	100	100	100	—	[54]
40	75	92	100	100	100	—	[267]
—	30	45	91	100	100	—	—
—	47—100	—	90—100	100	100	—	[90]
—	30—40	65—80	90—95	100	100	—	[62,58]
—	20—30	—	95—100	100	100	—	[11]
—	—	—	—	60	90	Catalyst is stable to heat in a stream of air at 900-950°	[129]
—	—	—	91	96	97	Catalyst is stable to heat (900-950°), surface remains unchanged	[128, 130]
—	60—65	96	100	100	100	—	[62, 113]
60	98	100	—	—	—	—	[110]
—	100	—	—	—	—	—	
—	20—40	40	75—90	95—100	100	—	[58,62]
—	35—62	—	85—96	95—99	—	—	[91]
—	—	—	45—75	—	90—95	—	[86]
—	98	99	99,6	99,6	—	—	[91]

Continuation of Table 5

1	2	3
$\frac{CuO \cdot MnO_2}{Al_2O_3}$ (3:1, 34% oxides on support)	1% CO in air	18
Manganese ore of Nikopol' deposit	"	18
Kazakhstan copper ore, malachite, chrysocolla	"	36
Aktyubinsk chromium ore	"	"
Manganese ore of Nikopol' deposit, activated with 10-20% CuO	"	"
	Exhaust gas: 16-17% O_2, 1-3% CO_2, 2.5-5.6% CO, 0.008-0.013% acrolein	
Ferromanganese activated with CuO	Exhaust gas: CO 0.1-2.7%, aldehyde 0.0008-0.01%, nitrogen oxide 0.005-0.006%	Fluidized bed, thickness of catalyst bed 25-30 cm
Pyrolusite + dunite + CuO (1:1:1)		
Dunite activated with MnO_2 + CuO	"	"
Dunite + NiO	"	"
Dunite + NiO + MnO	"	"
Ferromanganese + dunite + CuO	"	"
Homogeneous catalyst: 3.0 g/l Pd^{+2}	0 3—2% carbon monoxide in air	0,8
Fe^{+3} - 1.1 g/l		1,6
Cl^-/Br^- = 0.2		
CH_3COO^- = 13,1 g/l		2,4
Cu^{+2} = 14,1 g/l		

Continuation of Table 5

4	5	6	7	8	9	10	11
35—50	78—98	100	100	100	—	Water vapor up to 5% has no deactivating effect on catalyst	[113]
—	20—60	—	73—87	92—99	100	Stable in long-term operation	[114]
—	70—75	80—85	85—90	98—100	100		[58]
—	20	45—50	65	85	92		•
—	35	—	79	92	95		•
27—39	53—67	—	89—99	98—100	100	Stable in operation with 5% water vapor	[114]
—	11—83	—	80—96	87—93	92—97	Up to 60-70% of nitrogen oxides and 70-80% acrolein removed on the contact at 200°	[114]
—	—	—	—	74—99		Aldehydes oxidized completely; content of nitrogen oxides remains unchanged	[115]
—	—	—	—	60—78	—		•
—	—	—	—	90—99	—	Aldehydes 20-60% oxidized, amount of nitrogen oxides increases	•
—	—	—	—	80—100	—		•
—	—	—	—	90—97	—		•
—	—	—	—	75	—	Acrolein and formaldehyde oxidized completely, nitrogen oxides remain unchanged	
Complete oxidation is achieved at 20°						New method of catalyst regeneration with simultaneous oxidation of CO has been proposed.	[50, 51 58, 60]
75 % at 20°							
50 % at 20°							

Houdry. In 1950, he proposed a platinum catalyst, an "oxicat" consisting of platinum specially deposited in layer (0.05 mm) on a porcelain carrier pretreated with ground colloidal aluminum oxide. The catalyst was found to be stable when used for 1600 hr in an automobile. He also developed a catalyst for purifying the exhaust gases of automobiles operating on ethyl gasoline. Unfortunately, the laboratory data on this work have not been published in the literature. Soon thereafter, a platinum catalyst on a ceramic carrier was designed for this purpose in the USSR, and later, on an aluminum oxide carrier, mechanically strong samples of which are made in the form of rods and beads according to a method developed by the Karpov Physicochemical Institute [17, 20].

The removal of carbon monoxide from artificial mixtures and exhaust gases on platinum catalysts occurs readily. At a platinum content of 0.2-0.5 wt.%, carbon monoxide oxidizes to the extent of 20-30% at 200°C., and at 300°C. a complete oxidation is observed over a wide range of space velocities of the gas flows (up to 120,000 1/1 of catalyst per hour).

Among the plant catalysts tested, a high degree of activity in the reaction of oxidation of carbon monoxide is displayed by the AP-56 platinum catalyst in both the initial and used form, palladium-ruthenium [267] and copper-chromium catalysts [62]. However, the mechanical strength of these contacts is low. On the platinum and copper-chromium catalysts, hydrocarbons and soot burn completely together with carbon monoxide at 500°C. and above. The palladium-ruthenium catalyst in a reducing atmosphere is known as a catalyst for the removal of nitrogen oxides and hydrocarbons from gases [440].

The drawbacks of platinum catalysts are their high cost and the scarcity of Pt throughout the world, and also their inability to bring about the reaction of complete oxidation of carbon monoxide and hydrocarbons at temperatures below 150-200°C. This is the temperature range of the exhaust gases of idling engines, when the bulk of unburned components of the fuel are discharged. Still unexplained is the role of the platinum catalyst in the processes of decomposition of nitrogen oxides in oxygne-containing gas mixtures.

Not as scarce and more accessible and cheaper is the palladium catalyst, first investigated by O. M. Todes et al. [85]. The authors of this paper and later D. V. Sokol'skiy et al. [54] showed the great activity of the palladium catalyst on a carrier in the oxidation of carbon monoxide in air. At space velocities up to 30 x 10 hr^{-1} in a stream of air, this catalyst achieves a 100% oxidation of carbon monoxide to carbon dioxide even at 200°C. The paper [54] described a comprehensive study of the oxidation reaction of carbon monoxide both in the liquid phase [50, 51, 58] in the presence of palladium ions, and at a high temperature in the presence of palladium, platinum and mixed palladium-platinum and palladium-ruthenium catalysts on carriers [54, 56-61, 267]. In addition to studying the kinetics and mechanism of this reaction, the authors were interested in the possibility of a practical application of the catalysts to the removal of carbon monoxide from exhaust gases.

Particular attention was focused on the methods of preparation of highly active, stable, mechanically strong and easily regenerable palladium caatlysts. A number of new methods for preparing contacts and carriers of different chemical types and structures were used for this purpose. As a result, new methods of preparation were proposed, along with new compositions of palladium and mixed catalysts with a controllable depth of impregnation, for the purpose of removing carbon monoxide from gasoline and diesel engine exhausts. A special chapter is devoted to a discussion of these data.

In addition to metal contacts (platinum, palladium, ruthenium, silver) on carriers for oxidizing carbon monoxide, oxides of many transition elements mixed with one another, on carriers, or in the form of spinels, are widely employed for the oxidation of carbon monoxide.

Among oxide catalysts, the copper and iron-copper catalysts on carriers [62, 110, 113], copper-chromium [62, 90], manganese-copper catalysts of the type of hopcalites [86, 113], manganese-iron [91], and copper-chromium catalysts on carriers [62] have been thoroughly investigated. A detailed analysis of the results of oxidation of CO obtained in their presence and of the mechanism of their action is given by D. V. Sokol'skiy and G. K. Alekseyeva [58, 62], M. S. Belen'kiy and M. Yu. Sultanov [157], and others.

The data listed in Table 5 attest to the high activity of oxide catalysts under laboratory conditions. A particularly high activity, comparable to that of platinum and palladium at space velocities of 36-72 x 10^3 hr^{-1}, is displayed by copper oxide and copper-chromium catalysts [58, 62, 90, 110, 113, 131]. In their presence, carbon monoxide is 50-100% oxidized even at 200°C. (Fig. 10, 11).

In the case of oxidation of carbon monoxide on copper oxide without a carrier, the method of preparation is very important. Addition of an alkali (KOH) decreases the rates of adsorption and oxidation of carbon monoxide and increases the adsorptive capacity of the contact for carbon dioxide - the reaction product, thereby slowing down the process [144]. Copper oxide catalysts are poisoned by water vapor. Cohen and Nobe [159], who studied the effect of water vapor on the oxidation of carbon monoxide at space velocities of 10 x 10^3 hr^{-1}, showed that even slight concentrations of water vapor strongly decrease the activity. Increasing the water vapor concentration above 800 parts per million has practically no effect on the activity of the contact.

The activity of copper-chromium oxide catalysts is determined by the quantitative ratio of the oxides and their content on the carrier, and it is maximum at a Cu:Cr_2O_3 ratio close to 1:2 [62, 58, 90], when they form a spinel.

The special properties of other spinels are indicated in the paper [91], which notes their high activity in the oxidation reaction of CO at space velocities of 2.4-4-6 x 10^3 hr^{-1} and a CO concentration of 2-6%.

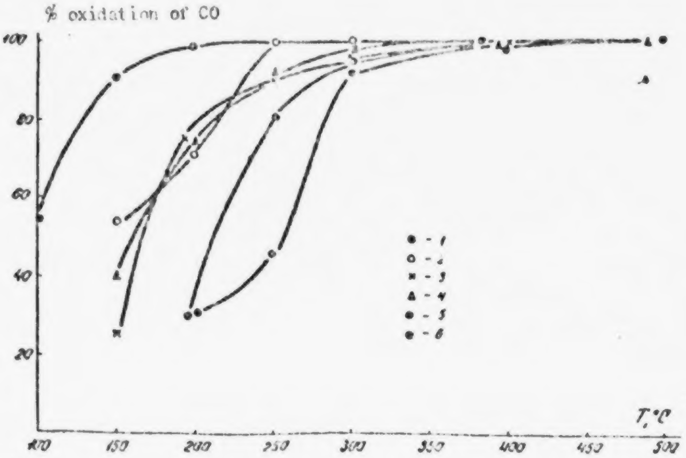

Fig. 10. Oxidation of 1% CO in a stream of air at a space velocity of 36 x 10^3 hr^{-1} on commercial catalysts.
1 - used AP-56; 2 - Fresh AP-56; 3 - copper-chromium-barium catalyst;
4 - NPK-1; 5 - ROSh; 6 - GIPKh-105.

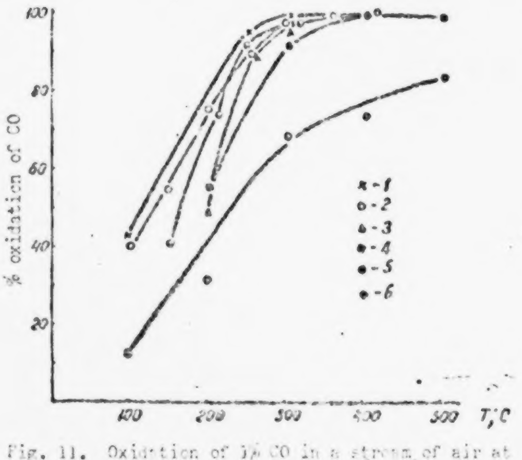

Fig. 11. Oxidation of 1% CO in a stream of air at a space velocity of 36 x 10^3 hr^{-1}.
1 - Pd/Al_2O_3; 2 - KRA-5; 3 - Pt-Pd/ShAS-2; 4 - Fe-Cu oxide catalyst on clay; 5 - Cu-Mn oxide catalyst/Al_2O_3; 6 - Pd-Ru.

It has been shown that at 400-500°C., the degree of oxidation of carbon monoxide on manganese ferrite, copper manganite and chromite, and manganese chromite is 91-100%. As the temperature is lowered to 200-300°C., spinels form the following sequence from the standpoint of the degree of oxidation: copper manganite (98-99%), copper chromite (77-98%), manganese ferrite (62-96%), and magnanese chromite (11-70%).

The copper-chromium catalyst has shown a high stability in prolonged testing in the laboratory at temperatures above 500-600°C., and served for 620 hours without any appreciable decrease in activity [131].

T. G. Alkhazov and M. S. Belen'kiy made a thorough study of the oxidation of carbon monoxide on an iron oxide catalyst on aluminum oxide [158, 130, 128, 129]. The maximum activity is reached at 1-2% Fe_2O_3 in the contact: at 200°C., 51%; 250°C., 30%; 300°C., 70%; 350°C., 90-95%.

The above authors note [129] the high stability of the iron oxide-aluminum catalyst during heat treatment (900-950°C. for 5-25 hours). This catalyst withstood tests during oxidation of carbon monoxide in gases from the regeneration of petroleum cracking catalysts [128]. It was shown that the most suitable carrier is plant aluminum oxide.

Researchers have been particularly interested in the possibility of using hopcalite for removing CO from exhaust gases, and also mixtures of copper and manganese oxides similar in composition to hopcalite [113, 91]. The activity of copper manganite (see Table 5) was high; starting at 200°C., carbon monoxide was virtually completely oxidized on this catalyst. This showed it to be similar to hopcalite, which operates at low and even subzero temperatures. However, hopcalites, copper oxide-manganese oxide and other oxide catalysts, for example copper and copper-chromium ones, are very sensitive to the action of water vapor and quickly lose their activity [21-162] when used to remove CO from exhaust gases and mixtures containing substantial concentrations of water vapor.

When oxides of copper and of copper and manganese are deposited on a carrier, they become more resistant to the action of moisture [113]. It has been shown that a water vapor content of up to 5% in a mixture of gases does not reduce the activity of the copper-manganese catalyst on bentonite clay. In hopcalite deposited on bentonite clay, the mechanical strength simultaneously increases [116], which is very important for the pratical application of oxide catalysts of relatively low mechanical strength. In addition to improving their stability to moisture, the use of these contacts on carriers increases their resistance to sintering, to a reduction of surface area at high temperatures, and to the formation of metal beads during oxidation of large concentrations of CO and hydrocarbons.

The stability of manganese oxide and copper oxide catalysts to water vapor can also be increased in another way, i. e., by promoting them with platinum, palladium, or silver oxides. Thus, a series of patents [121-124, 285, 363] indicate the promoting influence of silver, palladium and their mixtures, and the moisture resistance of promoted oxide catalysts.

Katz and Halpern [120] have shown that when silver nitrate is added to manganese catalyst during its preparation, a stable catalyst is obtained. A high moisture content (up to 80%) favors the oxidation of carbon monoxide. At the same time, it is important to deposit the mixture on a carrier (kaolin, talc, asbestos).

In a study of the oxidation kinetics of carbon monoxide on manganese-containing catalysts at low temperatures and pressures, it was observed [117] that the strongest activating effect among the additives studied (Pt, Ag, CuO, Fe_2O_3, V_2O_5) was displayed by platinum. An electron-microscopic study of the catalyst established that platinum spreads in a thin film over the surface of manganese dioxide. The authors hold the view that Pt and MnO_2 act as two independent catalysts: carbon monoxide is adsorbed on the platinum surface, and this in turn accelerates the process of activation of oxygen on MnO_2. A similar separation of the functions of the individual components of mixed oxidation catalysts appears possible in an intimate adsorptive but not chemical interaction of the components. A fact of this kind was observed and thoroughly investigated by Royter et al. in the oxidation reaction of hydrogen [118, 119, 160]. It was shown that platinum accelerates the donor process (activation of H_2), which is the rate-determining step in the oxidation reaction of H_2 on vanadium oxides, which proceeds in accordance with an electron mechanism. Platinum promotes the activation of hydrogen by dissociating the molecules into atoms and H^+ ions, which because of their high surface mobility migrate to areas of vanadium oxides adjacent to the platinum. This facilitates the reaction of hydrogen with oxygen activated on the vanadium oxides.

The promoting of oxide catalysts may lead to a change in the kinetics and mechanism of the process [160]. No positive effect was observed by mixing platinum and vanadium oxide mechanically.

Very similar results are obtained by promoting low-percentage vanadium oxide (1.5 wt.% V_2O_5), cobalt oxide (0.5 wt.% cobaltous-cobaltic oxide) and cerium oxide catalysts on aluminum oxide with palladium in the oxidation reaction of carbon monoxide.

Figures 12, 13 and 14 present comparative data on the oxidation of 1% of carbon monoxide on cerium dioxide deposited on beads of aluminum oxide, and on catalysts with 0.5 wt.% cerium promoted with 0.05% palladium at space velocities of 36×10^3 hr^{-1} (Fig. 13) and 72×10^3 hr^{-1} (Fig. 14). The palladium was precipitated on low-percentage oxide catalysts by chemical means.

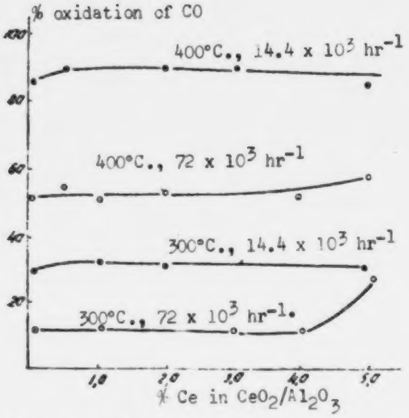

Fig. 12. Oxidation of 1% CO in a stream of air on cerium oxide catalysts on aluminum oxide at a space velocity of 14.4-72.0 x 10^3 hr^{-1}.

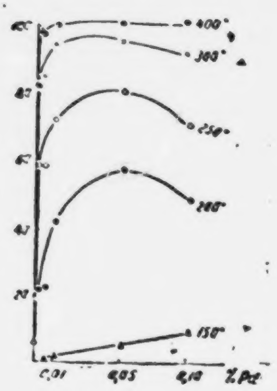

Fig. 13. Promoting effect of palladium on the oxidation process of 1% CO in a stream of air (36 x 10^3 hr^{-1}) over a cerium oxide catalyst on bead aluminum oxide (0.5 wt. % CeO_2).

It is obvious from the data shown in Figs. 12, 13, and 14 that a mutual promoting effect is displayed in the case of mixed contacts. The observed effects probably have a rational explanation only if one distributes the functions among the various active surface centers of the mixed catalysts. The acceleration of one process, for example, activation of carbon monoxide on palladium atoms added to the cerium oxide catalyst on the carrier, increases the electron concentration in the catalyst and facilitates the acceptor stage of the process, i. e., the activation of oxygen on the metal oxides with formation of oxygen ions. There is no doubt that the promoting causes a substantial change in the binding energy of the adsorbed substances, i. e., oxygen in the reaction under consideration. It is known that the energy binding oxygen to the surface of oxides, spinels and metal catalysts has a decisive influence on their activity in oxidation reactions of carbon monoxide, hydrogen, and hydrocarbons [147, 161, 163, 164, 186].

The use of a mixed palladium-cerium oxide catalyst on aluminum oxide substantially lowers the temperature of the process: even at 200-250°C., a 60-80% oxidation of carbon monoxide in the stream of air is observed. The high activity of low-percentage cerium oxide catalyst on aluminum oxide in the oxidation reaction of carbon monoxide is not unexpected. Rienacker has shown that at a ratio of cerium dioxide: aluminum oxide = 3:4, this contact manifests a catalytic activity in this reaction at 200-300°C. A 100% oxidation of carbon monoxide at 270°C. is also possible on a thorium oxide - cerium oxide contact [135]. The observed strong oxidizing properties of cerium oxide catalyst are explained by the low binding energy of the adsorbed oxygen, which is comparable in mobility to oxygen adsorbed on cobaltous-cobaltic oxide [408]. As a result, during the oxidation of carbon monoxide on cerium oxide catalyst, the process is inhibited by a slight adsorption of carbon monoxide (activation energy, 10-12 kcal/mole). Promoting of the catalyst with palladium facilitates the donor step, and the reaction proceeds at a lower activation energy (6.5 kcal/mole). Recently, Barrett et al. [181] obtained a patent on a mixed cobalt oxide - cerium contact (8.6% CeO_2 and 8.8% Co) on aluminum oxide, recommended for the oxidation of carbon monoxide and hydrocarbons.

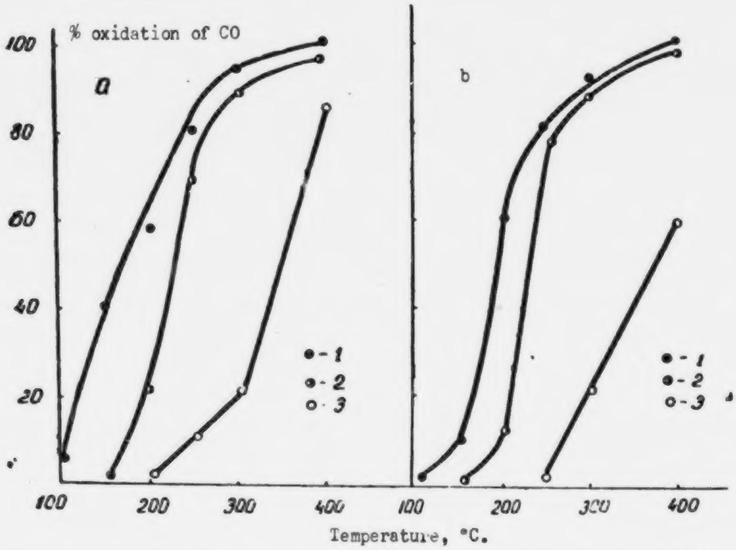

Fig. 14. Comparative oxidation of 1% CO on cerium oxide (0.5 wt. %, curve 3), palladium (0.05 wt. %, curve 2), and cerium oxide--palladium catalysts (0.05 % Pd, 0.5 wt. % CeO_2, curve 1) at a space velocity of 36×10^3 hr^{-1} (a) and 72×10^3 hr^{-1} (b)

A survey of the extensive patent literature on the catalytic purification of exhaust gases shows that in addition to platinum and oxide catalysts, other catalysts have found broad applications: mixed supported catalysts (on aluminum oxide, silica-alumina, etc.) consisting of oxides of polyvalent metals (copper, chromium, vanadium, molybdenum, manganese, cobalt, nickel) in the proportion of 0.5-25 wt. %, with platinum, palladium, iridium, rhodium, and silver as promoters [123, 124, 125, 126]. The introduction of salts of phosphoric acid and phosphoric acids themselves into the composition of the catalysts [126] increases their stability to lead and facilitates the regeneration.

In recent years, there has been a marked increase in the researchers' interest in natural materials: refractories (dunite), copper, chromium, manganese and ferromanganese ores in various deposits. As is evident from collective Table 5, "natural catalysts" possess a high activity in the reaction of carbon monoxide oxidation, particularly when activated with oxides of copper, nickel, manganese, and silver [58, 92-94, 114, 115, 127]. Copper and chromium ores of the Kazakhstan deposits, malachite, Aktyubinsk chromium ore and manganese ore of the Nikopol' deposit at space velocities of 18-36 x 10^3 hr^{-1} yield a 50-70% oxidation of carbon monoxide at 200-250°C. (Fig. 15) in a stream of air. Despite the higher activity of pyrolusite and malachite, Atasu and braunite ores in the oxidation reaction of carbon monoxide, their value is decreased by their poor mechanical and heat-resisting properties.

Manganese ore of the Nikopol' deposit has a higher wear resistance. The activity of manganese ores increases considerably when they are activated with copper oxide (3 wt. %) and silver (0.5 wt. %) and they can be used for purifying the exhaust gases of thermal drilling rigs and in other processes at lower temperatures (150-200°C.). The activation of manganese ores with copper oxide increases their stability in long-term service and in the presence of up to 5% water vapor [113]. Natural manganese ores activated with copper oxide promote the oxidation of hydrocarbons in addition to that of CO, the oxidation of aldehydes (up to 70-80%), and the elimination of nitrogen oxides (up to 70%) [395].

In selecting the ore and carrying out the activation of copper oxide and silver salts with it, the method and conditions of thermal treatment become significant. It is important to obtain and select an ore with the maximum content of pyrolusite, a β modification of MnO_2, the promoting of which yields a greater effect than that of α-MnO_2.

Decreasing the content of nitrogen oxides in mixtures after purifying the exhaust gases in the presence of manganese ores assumes a major importance, since no other methods of removing nitrogen oxides from oxygen-containing mixtures exist to date. The purification probably is also partly due to absorption of nitrogen oxides by the ores with formation of manganese and iron nitrates, which are capable of dissociating (decomposing) at higher temperatures (above 300°C.). It is necessary to explore the mechanism of the process and to determine the service life of such a catalyst.

In addition to the development of heterogeneous gas-phase catalysts for oxidation of carbon monoxide, a homogeneous catalyst has been proposed [50, 51, 58-60, 75]. The composition of the catalyst includes ions of palladium, iron, copper, chromium, bromine, and acetic acid in certain proportions. At the optimum relative amounts of the components, the catalyst completely oxidizes 1% CO in a mixture at 20°C. at a space velocity of 800 1/1 of catalyst per hour (Fig. 16).

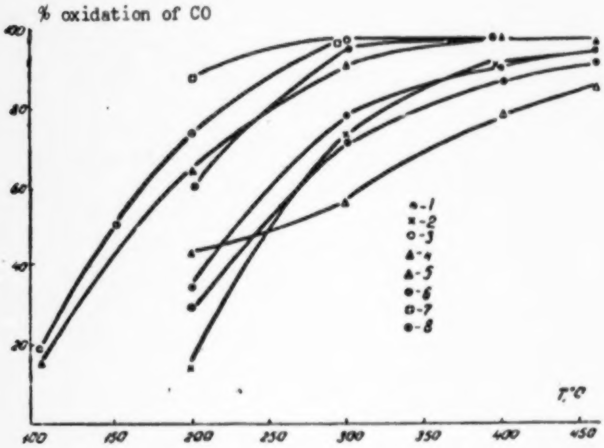

Fig. 15. Oxidation of 1% CO in a stream of air at a space velocity of 36 x 10^3 hr^{-1} in the presence of manganese and chromite ores [62, 114, 395]. 1 - Aktyubinsk chromite ore; 2 - Manganese ore of Nikopol' deposit; 3 - same, promoted with 3% copper oxide; 4 - same, promoted with 0.5% silver oxide; 5 - chrysocolla; 6 - malachite ore; 7 - pyrolusite; 8 - Atasu braunite ore.

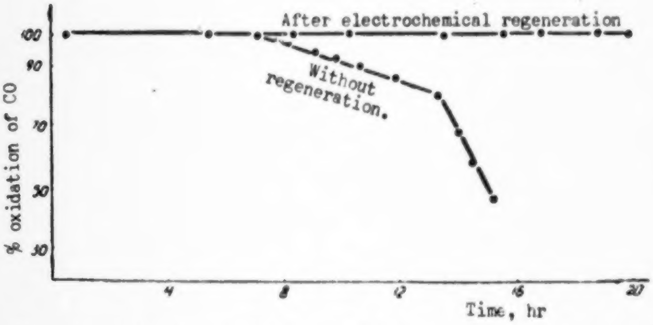

Fig. 16. Oxidation of carbon monoxide in the presence of palladium complexes in solution at 20°C. and a space velocity of 800 hr^{-1} with electrochemical stabilization of the catalyst [50].

A low-temperature homogeneous catalyst for oxidation of carbon monoxide can be used successfully in plants and units where high temperatures are unsafe (coal mines, cleaning ventilation units). An improvement of the design of the device (the reaction occurs under foam conditions) will raise the efficiency of the catalyst and increase the space velocities of the gas flows.

Judging from the available data, natural manganese ores activated with copper or silver oxides appear to hold promise as inexpensive catalysts for purifying exhaust gases containing CO, aldehydes, hydrocarbons, and nitrogen oxides at low temperatures. Tests of their activity and operational stability in streams of exhaust gases should be accelerated on internal combustion engine stands. Thus, in addition to platinum and mixed catalysts of group 8 metals and also palladium and supported oxide catalysts promoted with platinum group metals, of interest for the practical removal of carbon monoxide from exhaust gases may be natural ores activated with metal oxides including oxides of precious metals.

Chapter 3

OXIDATION OF CARBON MONOXIDE ON LOW-PERCENTAGE METAL CATALYSTS

A survey of the literature on catalytic removal of toxic components from exhaust gases shows that the most suitable catalysts for this purpose are low-percentage supported metal catalysts.

Because of the rigid conditions of operation of exhaust-purification catalysts (high space velocities of up to 100×10^3 hr^{-1}, overheating to 800-1000°C., stable activity for no less than 20,000 km) there follow some special requirements with regard to the methods of their preparation. First of all, the catalyst must be effective, stable to thermal treatment over a wide temperature range, and must be characterized by a strong adhesion between the metal and the substrate and an optimum depth of impregnation of the carrier. Of particular importance is the choice of the carrier, whose chemical nature and structure determine the activity and operational strength of the catalyst. There is need for simple methods of catalyst regeneration in the course of operation and recovery of precious metals from the spent contacts.

The section below discusses the development of a method of preparation of platinum, palladium and mixed supported catalysts suitable for oxidizing carbon monoside and other components of exhaust gases. Particular emphasis is placed on the method of deposition of metals on the carrier, the conditions of preliminary activation of the contacts, and effect of the carrier on the activity and mechanical strength of the catalysts.

Methods of Preparation of Catalysts

There are a number of methods of preparing catalysts for oxidation-reduction processes in the form of supported metals. They include:

1. Precipitation of metals from solutions of their salts or other compounds, followed by roasting and reduction.
2. Deposition of the metal layer by brazing from organic pastes.
3. Electrolytic deposition of metal on metal or on a conducting layer previously deposited on the support.
4. Preparation of cermets by sintering.
5. Deposition of a metal layer by cathodic vaporization in a vacuum.

In practice, two variants of the first method have been most widely adopted: adsorption by the carrier of compounds of active metals from dilute solutions with removal of excess solution (adsorption catalysts) and impregnation of the carrier with solutions of salts based on its moisture capacity.

The second variant is simpler and more convenient, since in some cases the steps of filtration and washing of the contacts are eliminated.

Usually, the carriers (Al_2O_3, silica gel, aluminosilicate, etc.), from which the moisture has been removed by drying, are impregnated with solutions of salts of the corresponding metals, the moisture is driven off at 110-120°C., and reduction to metals is carried out in a stream of electrolytic hydrogen at 200-500°C. Platinum, palladium [187-202] and palladium-ruthenium contacts [203] are thus obtained for use in the removal of O_2, NO and C_2H_2 from converted gas.

Complex salts of platinum metals are decomposed to the metals by firing at a high temperature. Thus, in the work of Kh. M. Minachev and N. I. Shuykin et al., active Pt, Pd, and Re-Pd reforming catalysts were prepared by impregnation of the carrier with solutions of the corresponding complex salts or acids, followed by roasting [192, 193] or by treatment with hydrogen sulfide at low temperature [234-238]. The activity of such contacts is positively affected by the addition of compounds of group III metals and rare earth elements to the impregnating solution [242]. In the deposition of platinum on nonporous carriers, the binder used by some authors is a mixture consisting of an aqueous suspension of finely ground aluminum and beryllium oxides with an admixture of aluminum nitrate [239-241]. Metal films strongly bound to the base are thus formed.

The activity and stability of contacts obtained by impregnation are greatly affected by the nature of the initial salt. Thus, a study by M. D. Adamenkova and O. M. Poltorak has shown (Table 6) that in the decomposition of hydrogen peroxide, the greatest activity among platinum contacts on silica gel is displayed by a catalyst prepared from a platinum ammine [227].

Table 6

Effect of the Nature of the Initial Platinum Salt on the Catalytic Activity of Platinized Silica Gel Samples [227].

Initial Platinum Compounds	% Adsorption of Salt on SiO_2	% Pt on SiO_2	$T_{red.}$ °C	$\frac{K_1 \cdot 10 \text{ mg}}{\% \text{ Pt}}$
$(CH_3NH_2)_4PtCl_2$	72	1,44	150	0,028
$(NH_3)_4Pt(NO_3)_2$	36	0,73	200	0,178
$[(NH_3)_4(OH)_2Pt](NO_3)_2$	36	0,73	200	0,147
$[(NH_3)_4(OH)_2Pt](Cl_2)$	83	1,67	200	0,065
Platinum ammine, series I (drying for 3 days at room temp., then at 65°C.)	95	1,50	300	0,290
Platinum ammine, series II (drying at 65°C.)	95	1,50	300	0,690

Platinum contacts prepared from $[Pt(NH_3)_4](OH)_2$ display a high stability during petroleum cracking [228] (Table 7).

Table 7

Activity and Stability of Petroleum-Cracking Platinum Contacts

Initial Platinum Compound	Platinum Content, %	Reduction in Octane Number	Overall Stability Index
H_2PtCl_6	0,48	2,5	53
$[Pt(NH_3)_4]Cl_2$	0,454	4,0	43
$[Pt(NH_3)_4](OH)_2$	0,465	2,0	82

Other researchers [229] also indicate a high stability of platinum, palladium, and rhodium oxidation, hydrogenation, cracking, and reforming contacts prepared by impregnating aluminum oxide with solutions of organic metal complexes containing no chloride ions.

In order to obtain a very uniform and strong coating of Pt, Pd, Rh, Ru, Ag, or their mixtures (Pt-Rh, etc.) on the aluminosilicate carrier, it is recommended that the catalyst be reduced while still moist (15-20% moisture content) at a low temperature (up to 75°C.) with subsequent roasting in air at 100-1000°C. [204]. The same effect is produced by the introduction of oxidants into the impregnating solution. In US patents, it is recommended that in the precipitation of platinum from chloroplatinic acid solution on aluminum oxide, the oxidizing agents used be nitrates (nitric acid, 0.3-1.5 times the weight of the platinum) or hydrogen peroxide [209, 210].

In some studies, the carrier is first impregnated with solutions of salts of metals, for example platinum and ruthenium [205], which are then precipitated with sodium carbonate in the form of hydroxides. Lacev [206] proposes that after the carrier has been impregnated with sodium carbonate, the metal (Pt, Pd, Rh, Os) compound be deposited during boiling from organic solutions (ketones). The metal oxide, which thus deposits only on the outer surface of the carrier, is dried after the ions of the initial salt are washed off and is reduced in nitrogen-hydrogen mixtures at 250°C. [201, 202, 398].

A rapid reduction of the metals from the salts and formation of an active metal layer is facilitated by a preliminary treatment of the carriers with hydrogen or carbon monoxide [207, 208]. A positive effect on the reduction rate is produced by the introduction of formaldehyde into the stream of hydrogen. Active palladium and platinum catalysts on asbestos fabric and porous ceramic rings for industrial applications are thus obtained [77, 84, 211-213]. The method of preparation of supported metal catalysts is substantially simplified by reducing the metals from their salts with the aid of reducing solutions that impregnate the carrier before or after deposition of the salt of the initial compound. The reductants used are formaldehyde [214-216, 219, 397], sodium formate [103, 197, 217, 218], sodium hypophosphite [219, 220], hydrazine [220-221], hydroxylamine [222], organic acids in the presence of ammonia and without it [225, 226], ethylene glycol [224], compounds of 1,4-dihydropyridine [223], or dialkyl sulfides [399]. The temperature of preparation of the catalysts is thus substantially reduced, thereby apparently causing the formation of metals in the form of fine crystals with a nonequilibrium form of faceting, and a large fraction of amorphous phase which is due to a decrease in the surface migration of the metal atoms on the carrier.

Reduction of palladium with sodium formate [217, 218], and of platinum and other metals of groups 8 and 1 with hydrazine and hydroxylamine [221, 222], is used to prepare active palladium, platinum and mixed catalysts for the purification of internal combustion engine exhausts. A necessary step in the preparation of these contacts is the washing of the catalyst to remove extraneous ions following the interaction of the reactants on the carrier, drying at 120-170°C., and roasting in a stream of air at 250-550°C. depending on the type of contact.

If the composition of the complex organometallic compound includes reducing agents such as the acetylene [230, 231], amine [233], alkyl, cycloalkyl and other radicals [229, 335], the process of preparation of the catalyst is even more simplified.

Thus, Bukhovets [230, 231] has shown that after impregnating the carriers with complexes of palladium chloride or platinic chloride with dimethylethynylcarbinol, heating to 130°C. is sufficient to decompose the complexes formed to the metals. The same method is recommended for preparing a platinum catalyst by starting with organic complexes of platinum of the general formula $(Me, R_n, Y_p)m$, where Me is a polyvalent metal (Pt, Pd, Rh), R is a hydrocarbon radical of variable structure, and Y is H or OM [229].

In order to increase the stability of platinum-palladium catalysts in the reaction of dehydrocyclization and aromatization, the carriers are impregnated with solutions of complex salts of platinum and palladium with alkali metals, for example, Na_2PdCl_4 or K_2PtCl_6 [199, 400]. Alkali metal ions have a stabilizing effect on platinum. The intensity of the bands of metallic platinum in the x-ray spectra of these catalysts decreases, although the average size of the platinum crystals remains unchanged [401].

Catalysts on metal carriers (screens, wires, sheet steel) are prepared by electroplating, contact displacement of metals upon immersion of metal articles into solutions of the corresponding salts, and chemical reduction.

The electroplating of platinum group metals has been treated in special surveys and papers [402-407], so we shall not dwell on this method. Let us note only that the electroplating of platinum is carried out from phosphate electrolytes, and that of palladium, from phosphate and nitrite electrolytes after special cleaning of the conducting surface [259-262]. A drawback of contacts obtained by electrolytic plating of surfaces is the weak bond between the metal layer and the support and a small surface area. Nevertheless, all-metal catalysts made of alloys of platinum with other metals and deposited on special strips of alloy steels find extensive applications, particularly abroad, in the catalytic purification of industrial waste gases [409-411].

In applying a catalytically active layer of metal on wires, screens, and spirals of pure metals (copper, aluminum, iron) or their alloys (nichrome, "fekhral" [a high-resistance alloy similar to Fecraloy] nickeline, manganin, etc.), the method of brazing from reducing organic mixtures is frequently employed [243-247, 254-258]. The same method is suitable for applying metal on nonconductors: ceramics, glass, mica, etc. [248, 249, 252, 253]. It is recommended that rosin, amyl acetate, synthetic resins such as polymethyl methacrylate, and alcohols be included in the composition of the reducing mixture.

N. Z. Kotelkov and M. S. Gershenovich [243-246] use this method for applying platinum and palladium on nichrome wire for the purpose of oxidizing hydrogen, carbon monoxide, methane, and sulfur dioxide in the analysis and purification of internal combustion engine exhausts [6].

A catalyst obtained by brazing from an organic mixture has an extended surface coated with highly dispersed fine crystals. However, as the contact continues to be used, sintering is observed, and the active phase is partially carried off the surface. The authors have described the composition of tinctures and the conditions of their brazing. Palladizing is carried out by taking 0.05 g of palladium in the form of a saturated solution of palladium chloride, adding 0.5 ml of pinene, 0.5 ml of alcohol, and a few drops of a concentrated ammonia solution of salicylic acid (which produces a wetting layer). The nichrome wire is first kept red hot for about 10 hours (to obtain an oxide layer), then immersed in the tincture and heated for 10-15 min at a moderate temperature to braze the mixture, and the temperature is raised to a red heat. The brazing process is repeated two to three times, and finally the contact is kept at a bright red heat for 30 min.

In the platinizing process, 1 g of platinum tetrachloride is dissolved in 3 ml of alcohol, and 10 ml of a saturated solution of boric acid in alcohol and 20 ml of a 1:1 mixture of turpentine and lavender oil are added. According to the authors' data, the contacts thus obtained prove to be hundreds of times more active in the dehydrogenation of cyclahexane and tens of times more active in the oxidation of hydrogen than ordinary platinum or palladium catalysts on asbestos (Zelinskiy's catalysts). This effect is due to the fact that the oxide crust on the surface of nichrome protects the thermally precipitated platinum from fusing with the metal of the base at very high temperatures.

Brazing of metals from pastes into ceramics, glass, quartz, mica, and plastics is used to prepare electrically conducting coatings and has been described by B. Ya. Kaznachey [250] and F. Ya. Yevteyev [251]. The composition of the platinizing paste includes 1 g of chloroplatinic acid, 3 g of ethyl alcohol, 10 ml of a saturated solution of boric acid in alcohol, and 20 ml of turpentine.

The binders used are essential (lavender) and vegetable oils (linseed, cottonseed, soy, castor) or a solution of rosin in turpentine. Prior to the application of the paste, the ceramic is etched in hydrofluoric acid (or a small surface is prepared mechanically), then cleaned, dried and calcined at 550-600°C. The layer of paste applied on the surface of the carrier (by dipping or with a brush) is dried to drive off the volatile matter, then brazed in ovens with strong ventilation. The process of brazing of silver to a ceramic, for example, begins at 600°C., but better results are obtained at 800-850°C. At this temperature, the flux is more actively bound to the ceramic, and this increases the mechanical strength of the bond. Thus, B. Ya. Kaznachey notes that after a triple brazing of silver, an effort of 50 kg/cm^2 is required to detach it from the ceramic. A layer obtained by brazing has a porous structure and possesses no bulk conductivity.

To prepare metallized glass electrodes, M. S. Zakhar'yevskiy [252], V. A. Rabinovich and O. V. Kurovskaya [253] used a mixture of 1 g of chloroplatinic acid in 10 ml of alcohol with 10 ml of a saturated solution of boric acid in alcohol and 20 ml of a rosin solution. The rosin is first dissolved in hot turpentine, cooled, and diluted with an equal volume of alcohol. It is recommended that the brazing be carried out in the flame of a burner. If metal carriers are used, the platinum or its alloy with other metals is also brazed in the flame of a burner, but after the preliminary application of a thin layer of Al_2O_3, ZrO_2 or any other refractory oxide [254].

The metallization of refractories is carried out in two steps [255]. First, the surface of the refractories is coated with a thin platinum film that firmly penetrates into the fine pores, and in the second step pastes that can contain up to 50 wt. % platinum are used. The metal content and paste viscosity are selected according to the porosity of the refractory so as to allow the formation of dense metal films without excess impregnation of the interior of the refractory. The compounds of platinum and other metals in pastes decompose to the metals in atmospheric air, the strongest bond being obtained on nonporous materials.

Heating is carried out at different temperatures depending on the base: ordinary sodium glass 570-625°C.; Pyrex, quartz glass 650-680°C.; glazed ceramics 675-760°C.; unglazed ceramics 760-845°C.

Apparently, platinum was applied in a similar manner on porcelain rods in the shape of candles by the American scientists Houdry and Hayes in the preparation of a catalyst for removing noxious impurities from internal combustion engine exhausts [256, 257].

When silver is used to metallize the carrier surface [258], the paste is prepared by coprecipitation in aqueous solution of reducible silver compounds with compounds of other metals (alkaline earths, etc.) that are irreducible on heating, followed by reduction of the silver at low temperature and the formation of a suspension in an organic liquid. A catalyst with an extended surface and a high activity is prepared by applying the paste on a support.

In the preparation of cermets, finely divided powders of metals, their oxides and other chemical compounds are mixed in the required proportions, then molded and subjected to sintering at a high temperature. The papers of Ternision [263] describe the use of alloys of platinum with nickel and metal oxides ($ZrO_2 \cdot CaO$), obtained by sintering (25% porosity), as catalysts for the afterburning of automobile exhausts, surface combustion of rocket fuel, synthesis of hydrocyanic acid by oxidation of an ammonia-methane mixture with air, and other chemical transformations.

The methods of application of a metal layer by cathode sputtering and vacuum deposition are employed rarely and for special purposes.

It is evident from the above survey that among the methods of preparation of low-percentage platinum, palladium and mixed catalysts, those deserving most attention are methods of impregnation of the carrier with solutions of salts of the corresponding metals or their mixtures with organic reducing agents for the purpose of excluding the stage of reduction of the oxides to the metals in the gas phase and obtaining a strong bond between the metal and the support. One of the variants of such procedures are the methods of preparation of palladium and mixed catalysts containing palladium proposed by D. V. Sokol'skiy, N. M. Popova et al. [266, 267]. A distinctive feature of the method of preparation of a palladium contact is the small number of steps involved, i.e., the absence of such steps as washing of the catalyst to remove extraneous ions and reduction in hydrogen.

The effect of the conditions of preparation on the activity of contacts in the oxidation reaction of carbon monoxide was studied in the course of development of the method. It was shown that the degree of conversion of carbon monoxide is affected by the duration of the impregnation and the conditions of activation chiefly at temperatures of 200-250°C. (Table 8).

Table 8

Effect of Conditions of Preparation on the Activity of Palladium Catalyst on Synthetic Aluminosilicate (0.5 wt. % Pd) in the Reaction of Oxidation of 1% CO in a Stream of Air, $V = 36 \times 10^3$ hr^{-1}.

Impregnation Time, Days	Treatment Following Impregnation	Degree of Oxidation of CO, %			
		200°	250°	300°	400°
1	Drying at 110°C., activation at 400°C. in a stream of air for 0.5 hr	0	50	84	95
2		35	65	84	96
3		20	64	84	89
4	•	15	52	82	89
5	•	10	40	83	90
2	Drying at 110°C., activation at 400°C. in a stream of 3% CO and 10% O_2 for 0.5 hr.	17	55	82	92

Figures 17 and 18 show thermograms of a palladium catalyst on synthetic aluminosilicate and aluminum oxide, obtained during a gradual temperature elevation (5°C./min) for undried (1) and dried (2) samples. From the Pd/Al_2O thermogram it is clear that a change in the weight of the samples occurs mainly at temperatures of 50-120°C. and 230-270°C. The granules of both samples of catalysts blackened considerably at 50-100°C.

The activity of palladium and mixed palladium catalysts is greatly affected by the gaseous atmosphere (Table 9) in which the process of catalyst activation takes place. Contacts obtained by activation in hydrogen are less active in the oxidation reaction of carbon monoxide.

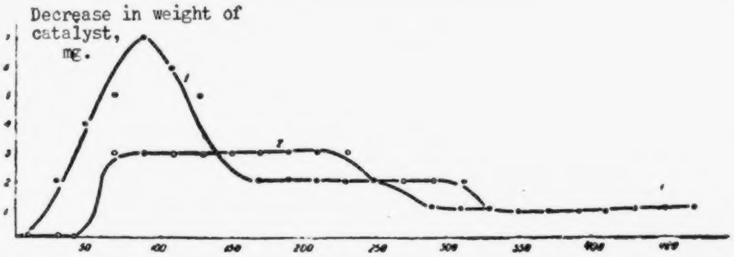

Fig. 17. Thermogram of palladium catalyst on synthetic aluminosilicate. 1 - sample before drying; 2 - sample from which moisture has been removed.

The temperature at which activation of the contacts takes place in the stream of air is of considerable importance. Table 10 lists data on the effect of the activation temperature on the oxidation of carbon monoxide over low-percentage platinum, palladium and platinum-palladium contacts.

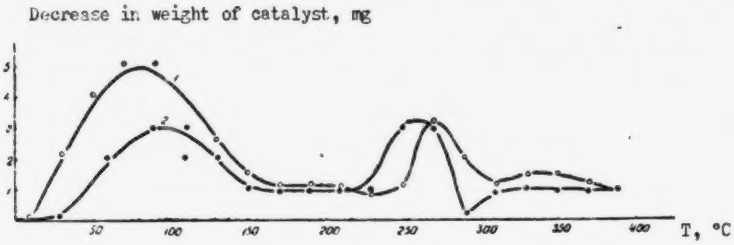

Fig. 18. Thermograms of palladium catalyst (0.5 wt. % Pd) or aluminum oxide. 1 -- sample before drying; 2 - sample from which moisture has been removed.

Experiments have shown that palladium catalyst on many carriers displays a maximum activity after activation in a stream of air for 3 hours at 400°C., and platinum catalyst, at 500°C. In the case of mixed contacts, the temperature of the treatment depends on the composition: for platinum-palladium and other platinum-containing contacts such as platinum-nickel and platinum-cobalt 500°C. is required, and for palladium catalysts, 400°C. The effect of the temperature of treatment of platinum catalysts and palladium foil with oxygen and an explosive gas mixture on their activity in oxidation-reduction reactions is discussed in [273-278]. In the hydrogen oxidation reaction, the activity of platinum increases almost linearly with rising activation temperature and rate of absorption of oxygen up to 550°C., then falls off linearly (Fig. 19) [274].

M. I. Nikolayeva and A. I. Shlygin [295] also observed that the rate of decomposition of hydrogen peroxide on thermally activated platinum goes through a maximum after it is treated at 500°C. This they explain by the formation of oxygen strongly bound to the platinum surface [295]. This was

Table 9

Oxidation of 1% CO in a Stream of Air in the Presence of Palladium-Cobalt Catalyst (Pd:CO = 1:1) ($\sum Me = 0.75$ wt. %) on Synthetic Aluminosilicate at a Space Velocity of 36×10^3 hr^{-1}.

Activation of Catalyst				Degree of Oxidation of CO, %			
In a Stream of H_2		In a Stream of Air					
Temperature, °C	Duration, hr.	Temperature, °C	Duration, hr.	200°	250°	300°	400°
300	4	—	—	20	42	60	77
300	2	—	—	10—22	30—45	60—74	77—88
500	1	—	—	12	48	60	77
400	1	—	—	15	31	60	80
—	—	400	0,5	22	37—54	60—74	75—88
—	—	400	2,0	10	26	42	64
—	—	400	2,5	15	47	70	80

Table 10

Oxidation of 1% CO in a Stream of Air at $V = 3 \times 10^3$ hr^{-1} on Platinum, Palladium and Platinum-Palladium Catalysts on Carriers (0.5 wt. %Σ Me)

Carrier	Percent of Carbon Monoxide Oxidation at Different Temperatures After Activation for 3 Hours in a Stream of Air at							
	400°				500°			
	200	250	300	400	200	250	300	400
Platinum/carrier (obtained by brazing platinum from an organic mixture for 2 hours in air)								
Corundum	67	74	100	100	77	100	100	100
Porcelain	21	50	100	100	96	100	100	100
Aluminum oxide	69	95	100	100	90	99	100	100
Synthetic aluminosilicate	76	100	100	100	79	100	100	100
Palladium/carrier (obtained by brazing palladium from an organic mixture in hydrogen)								
Aluminum oxide (reduced in H_2)	45	72	100	100	40	70	100	100
Synthetic aluminosilicate (not reduced in H_2)	0	35	65	95	0	18	43	92
Synthetic aluminosilicate (reduced in H_2)	36	68	100	100	28	62	100	100
Houdry catalyst (not reduced)	50	75	90	99	0	42	78	97
Keles bentonite clay	95	100	100	100	80	100	100	100
Platinum-palladium/carrier obtained by our proposed method								
Darbaza clay	75	98	100	100	90	100	100	100
Kustanay clay	46	77	100	100	60	95	100	100
Keles clay	43	71	100	100	67	84	100	100
Aluminum oxide	58	77	—	—	75	85	100	100
Ceramic	43	96	100	100	62	100	100	100

confirmed by Yu. M. Tyurin and L. G. Feoktistov [268], who noted an increase in the strength of the bond of oxygen adsorbed on platinum after activation of the latter at this temperature. V. P. Lebedev et al. attribute the maximum on the activity curves of platinum black and platinum on silica gel, starting from the calcination temperature, to the supersaturation of the surface with adsorbed oxygen [269-272]. M. Kraft and G. Spindler suggest that in the course of treatment of Pt/Al_2O_3 in a stream of air at 500°C., the finest particles of platinum either form a complex with oxygen, or oxygen enters the lattice of the fine crystals [302]. The penetration of oxygen atoms enters the lattice of the fine crystals [302]. The penetration of oxygen atoms into defects of the platinum lattice was noted by S. Z. Roginskiy and V. S. Rozing [277]. An extensive interaction of metals (particularly on carriers) with adsorbed oxygen causes some of the atoms to pass to a state that enables them (in contrast to massive platinum and palladium) to dissolve

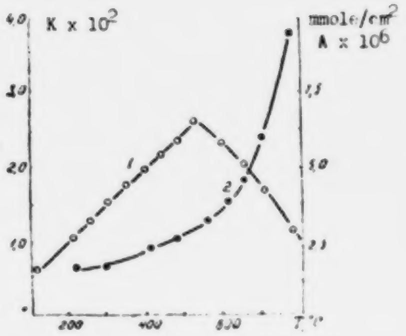

Fig. 19. Oxidation rate constant of H_2 on platinum vs. temperature of its activation with oxygen (1) and the amount of absorbed oxygen vs. temperature (2) [274].

in acids [412]. It is known that the binding energy between adsorbed oxygen and the metal determines its activity in oxidation reactions. Apparently, for platinum catalysts at 500°C. and palladium ones at 400°C., the conditions are favorable for the adsorption of oxygen of optimum binding energy which results in the maximum activity during oxidation of carbon monoxide.

In connection with the study of the effect of the conditions of preparation on the activity of low-percentage catalysts, it is of interest to compare the activity of contacts prepared by different methods. Table 11 lists data on the oxidation of carbon monoxide over platinum and palladium catalysts prepared by impregnating the carrier by our proposed method (method 1) and brazing of an organic mixture* by Kotelkov's method (method 2). The rate constant was calculated from a first-order equation. The specific rate constant was obtained by referring the rate constant to the amount of palladium in the catalyst.

Table 11

Oxidation of 1% CO in a Stream of Air at V = 36 x 10^3 hr^{-1} on Supported Palladium Catalysts (0.5% Pd) Prepared by our Proposed Method (Method 1), From an Organic Mixture (Method 2), and Activated in a Stream of Air at 400°C.

Carrier	Method	% Oxidation of CO			Weight of Catalyst, g	K 200°C	$K^{200°C}_{sp}$ x 10^3
		200°	250°	300°			
A-1 Aluminum	1	90	100	100	1.129	37,1	6,56
Oxide	2	45	72	100	1.301	9,56	1,47
Houdry Contact	1	54	80	100	1,072	11,7	2,19
	2	50	75	90	1,433	11,1	1,56
Bead Alumino-	1	60	90	100	1.324	14,7	2,23
silicate-2	2	36	68	100	1.503	6,1	0,81

The experiments showed that the specific activity of catalysts obtained by impregnation according to our proposed method was 2-4 times higher than in the case of brazing in a reducing atmosphere from a complex organic mixture.

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* The composition of the mixture included lavender oil, boric acid, ethanol, and α-pinene. Brazing was carried out in hydrogen for 2 hours at 250°C.

Table 12

Effect of the Method of Preparation of Palladium Catalyst on ShN-2 Bead Aluminum Oxide (0.5 wt. % Pd) on the Activity in the Oxidation Reaction of 1% CO in a Stream of Air at $V = 36 \times 10^3\ hr^{-1}$

Conditions of Preparation of Catalyst	Degree of Oxidation of CO, %				
	150°	200°	250°	300°	400°
Impregnation of aluminum oxide with a solution of $[H_2(Pd(NH_3)_4]Cl_2$, drying, activation at 400°C. in H_2 for 1 hr	12	43	71	91	98
Impregnation of aluminum oxide with a solution of $[H_2(Pd(NH_3)_4]Cl_2$, drying, activation for 2 hrs at 400°C. in a stream of air	27	57	76	86	99
Impregnation of aluminum oxide with sodium carbonate, then Na_2PdCl_4, followed by washing, drying, and activation for 2 hrs in a stream of air at 400°C.	27	65	76	91	99
Impregnation of aluminum oxide with Na_2PdCl_4, then sodium carbonate, followed by washing, drying, and activation in a stream of air at 400°C. for 2 hours	29	60	73	93	100
Impregnation of aluminum oxide with sodium carbonate, then Na_2PdCl_4, followed by washing, drying, and activation at 300°C. for 1 hr in H_2	32	68	79	94	100
Impregnation of aluminum oxide with a $PdCl_2$ solution, then sodium formate, followed by washing, drying, and activation at 400°C. for 2 hrs	30	60	80	94	100
Impregnation of aluminum oxide according to our proposed method followed by drying, and activation at 400°C. in a stream of air.	30—45	67—80	78—90	94—97	99—100

The activity of a palladium catalyst prepared by impregnation according to our method was found to be higher than that of contacts obtained by the known methods (Table 12). Palladium contacts prepared by reduction of palladium with sodium formate or precipitation with sodium carbonate have a similar activity, but their preparation is more complex. Activation of palladium in hydrogen decreases the percent oxidation of carbon monoxide. The preparation of palladium catalysts by impregnation according to our method followed by drying and heating has a number of advantages over the others: a single impregnation step and the elimination of the steps of reduction of the catalyst with hydrogen and washing off of extraneous ions.

Mechanical Strength of Catalyst and Depth of Impregnation of Granules

The mechanical wear and the exothermic oxidation reactions occurring on the surface loosen and break down the upper layers and structure of the catalysts, lower the content of active components, and lead to a decrease in the catalytic activity and service life of the contact. Exhaust purification catalysts are subjected to particularly strict service conditions as a result of the action of vibration during motion of the automobile and when they are in the form of a mobile layer after a partial breakdown and entrainment of the catalyst. For this reason, the mechanical strength of supported catalysts and the depth of penetration of the metal into the granules are of great importance in the production of low-percentage catalysts.

A major influence on the mechanical strength of low-percentage catalysts is exerted by the structure and size of the pores of the carrier. G. K. Boreskov, V. D. Dzis'ko, et al. have shown that in the case of aluminum oxide, the mechanical strength is determined by the conditions of its preparation and decreases sharply when the logarithm of the pore radius increases above 2.8 and when macropores predominate substantially over micropores [413].

The relative mechanical strength of palladium catalysts on ShN-2 aluminum oxide is affected by the mode of deposition of palladium on the carrier. Table 13 presents data on the relative mechanical strength of dried palladium catalysts (moisture content less than 0.5%) on Al_2O_3 as a function of the method of their preparation.* A high mechanical strength (90-93%) was displayed by contacts prepared by impregnation by the method we have proposed, especially when vacuum-dried and when the palladium was precipitated with sodium carbonate.

The mechanical strength of palladium catalyst on synthetic bead aluminosilicate ShAS-2 is affected by the conditions of drying and activation of the catalyst. The drying of the supported palladium catalyst must be carried out under equilibrium conditions at low temperatures (90-110°C.). Raising the temperature causes a marked difference between the partial vapor pressures of alcohol and water within the narrow pores of the bead aluminosilicate and in the air surrounding it, and causes the formation of microcracks in the contact pores which subsequently lead to a breakdown of the catalyst. Calcination and activation of the catalyst (after drying under equilibrium conditions) at high temperatures in a stream of air have no adverse effect on the mechanical properties of the catalyst.

The uniformity of distribution of the active metal on the carrier and the depth of impregnation are determined by the conditions of preparation of the contacts.

Usually, in catalysts obtained by impregnating a fabricated carrier, the metal distributes itself unevenly. According to the data of Rubinshteyn et al., this unevenness increases with the carrier grain size. The diffusion of the impregnating solution into the pores determines the degree of distribution of the metal over the carrier surface. If the diffusion rate is slow, the metal deposits at the entrance of the pores, particularly in the presence of reductants. A uniform distribution of the metal over the depth of the grain takes place if the carrier is kept in the solution or in the moist state for a long time following impregnation with solutions of the corresponding metal salts. When pellets of activated charcoal are impregnated with chloroplatinic acid then dried (120-125°C.) and reduced (330°C.), the bulk of the metal precipitates on the surface [279].

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* The relative mechanical strength of the samples was determined by attrition in a 250 ml bottle 2/3 full on a shaker at 600-700 osc/min for 5 hours. The amount of catalyst fractions remaining on a screen with d = 3 mm was taken as the measure of strength.

An x-ray absorption study of the distribution of platinum with depth in the grain has shown that as the depth of penetration into the grain increases, the metal contact in these catalysts decreases. A similar and still more pronounced uneven distribution of platinum and palladium within the grains has been observed in catalysts on aluminum oxide. The authors hold that the nonuniformity of the distribution of platinum in the carrier grains is due to a decrease in the concentration of the initial solution in the depth of the grain as a result of its adsorption by the surface layers of the carrier.

Table 13

Relative Mechanical Strength of Palladium Catalysts on Aluminum Oxide

Method of Preparation	Relative Mechanical Strength
Impregnation of carrier by our proposed method, vacuum drying	94
Impregnation of carrier with sodium carbonate followed by Na_2PdCl_4, washing, drying, and activation in a stream of air at 400°C.	93
Impregnation of carrier by our proposed method drying, and activation in a stream of air at 400°C.	90
Impregnation of carrier with Na_2PdCl_4, treatment with sodium carbonate, washing, drying, and activation in a stream of air at 400°C.	79
Impregnation of carrier with $[H_2(Pd(NO_3)_4]Cl_2$, drying, and activation at 400°C. in a stream of air.	76

Thus, in order to deposit the bulk of the metal in the surface layers of the carrier, it is necessary to use concentrated solutions of salts of the corresponding metals. Platinum distributes itself more evenly within the grain when dilute solutions are employed [280].

As the pH of the impregnating solution decreases upon introduction of organic or mineral acids (nitric, acetic) [281], the depth of penetration of platinum into the grain increases. By occupying a part of the accessible surface, the acids hinder the sorption of $PtCl_6^=$ anions and promote their diffusion into the pellet. An impregnation depth of approximately 2 mm is obtained in solutions of 2% nitric and acetic acids at an H_2PtCl_6 concentration of 2 g/l at 40-50°C. in 1-2 hours.

Obviously, the greater the depth of penetration of active metals into the carrier and the stronger the adhesion, the longer the time required for the contact to be used up, and thus its service life increases. However, a complete impregnation of the granules is also undesirable because of a decrease in the metal concentration in the outer layers, and also because the size of most stationary catalysts is limited by the size of the openings in the catalyst shelves. Exhaust purification catalysts are placed in the form of a thin layer between screens with a hole diameter of 2.5 mm. For an average size of carrier beads of 4-5 mm, the optimum impregnation depth is 1 mm.

The characteristics of our proposed method make it possible to control the depth of penetration of palladium into catalyst beads (from 0.1 to 2.5-3.0 mm) and to obtain low-percentage catalysts with a uniform distribution of the metal over the depth of the grain.

Regeneration of Precious Metals

Of no less importance than the process of preparation of low percentage catalysts is the regeneration of precious metals and palladium from catalysts. The question of recovering precious metals from spent contacts arises in connection with the complete deactivation of palladium and platinum reforming, platforming, isomerization, hydrogenation, and oxidation catalysts. The difficulty of carrying out this process sometimes lies in the fact that the deposited metal may react chemically with the carrier.

On the other hand, the peculiar state of adsorbed atoms on carriers in the range of high dilutions, consisting in a surface distribution that is intermediate between a metallic and an atomic distribution, facilitates their dissolution in acids without a simultaneous action of oxidants ($HCl + Cl_2$, $HCl + HNO_3$). Several authors have explained the ease of dissolution of platinum in low-percentage catalysts after treatment with air or oxygen by the conversion of a part of the platinum to a complex with the carrier where Pt exists in an oxidized state [302, 322].

The methods of extraction of platinum and palladium from ores, alloys and also spent catalysts may be divided into three groups: 1) extraction of precious metals by dry and wet chlorination; 2) dissolution of platinum and palladium in the presence of anodic polarization current; 3) extraction by chemical reaction with acids and alkalis with and without oxidants (chlorine, hydrogen peroxide, nitric acid). The extraction of precious metals by dried chlorination followed by dissolution in mixtures of acids is used mainly to extract platinum and palladium from ores and waste materials of low metal contant [283, 284]. The overall degree of extraction of platinum metals by this method is 89%; it is as high as 92% for platinum, but only 25% of palladium is recovered. When palladium-containing materials are treated with 2% HCl with an admixture of sodium chloride while a stream of dry chlorine is passed, the degree of recovery of palladium increases to 30-50% [301].

This method is used to extract platinum from concentrate with a high platinum content (25%), but dilute hydrochloric acid (1:1) is used, the stream of chlorine is at normal pressure, and the temperature is 90-95°C. Ore concentrates containing up to 5% of precious metal as chlorides are subjected to the action of a mixture of hydrochloric and nitric acids (refining), causing the formation of complex compounds of platinum and palladium.

The method of anodic dissolution of platinum, palladium and other metals of this group, for example rhodium, is applicable in the case of massive metal anodes or alloys [286, 287]. The anodic dissolution of palladium under the influence of a direct current is associated with considerable polarization and depends on the composition and pH of the solution and the temperature. A 100% dissolution of palladium is achieved in an aqueous solution of hydrochloric acid (1:1, 1:3) at a current density of 10 A/dm^2.

In the recovery of precious metals from catalysts, the latter are treated with an acid or a mixture of acids. Thus, N. V. Garmonov, A. L. Klebanskiy, and K. K. Chevychalova [288] recommend that palladium be separated from spent palladium catalyst on silica gel (used to hydrogenate vinylacetylene to divinyl) by dissolving in aqua regia then evaporating the solution, or in hydrochloric acid in the presence of chlorine. After the palladium had passed into the hydrochloric acid solution, the authors carried out the precipitation of palladium on silica gel by bubbling hydrogen through this solution.

There is a method of recovering platinum from a spent reforming catalyst (0.4-1.2 wt. % Pt, after the removal of organic impurities by calcination) involving treatment with sulfuric acid, which also dissolves aluminum oxide, followed by precipitation with polyacrylamide [290]. Other authors [291] recommend that the recovery of platinum from spent catalysts on aluminum oxide be carried out by dissolution in alkali under pressure.

A simpler method has been proposed by V. A. Klevke, D. S. Kantor and R. P. Seregina [289]. According to their data, the regeneration of palladium from spent palladium catalyst on aluminum oxide is carried out by treatment with dilute hydrochloric and nitric acids (10-36%) at the boiling point without the addition of chlorine.

D. V. Sokol'skiy et al. recovered palladium from a catalyst on aluminum oxide and aluminosilicate by heating in dilute nitric acid (1:1) to 40-50°C. (Table 14).

The regeneration of palladium from catalysts which have operated for a long time in gas purifiers of internal combustion engines takes place more slowly: a preliminary calcination of the contact is required in order to drive off the soot, and in some cases a mixture of nitric and hydrochloric acids must be used.

The precipitation of precious metals from solutions obtained in the regeneration of the compounds is based on methods of their chemical and electrochemical reduction, precipitation in the form of sparingly soluble organic compounds whose decomposition forms the metal black or oxide, and by means of selective adsorption on ion exchange resins.

Metals from solutions of salts of hydrochloric or nitric acid can be separated by evaporating down to a small volume, then adding a small amount of hydrochloric acid and sodium chloride in order to obtain complex sodium salts stable to hydrolysis [292]. Metallic palladium can be readily obtained from solutions of its compounds by reduction with formic acid, calomel, hydrazine, ethanol [293], and other compounds, for example, by passing reducing gases such as ethylene, carbon monoxide, and hydrogen through the solution. Similar methods are used for chemical separation of metallic platinum from solutions of its complex chlorides. A greater practical importance is assumed in this connection by a method proposed in a West German patent [294], whereby palladium-containing acid solutions are passed from the top downward through a column filled with packing coated with a layer of platinum or palladium. A stream of hydrogen entering the bottom of the column is simultaneously passed through it.

Table 14

Recovery of Palladium in Dilute Nitric Acid (1:1) From 50 g of Bead Catalysts Pd/ShAS-2 (0.75 wt. % Pd) and Pd/Al_2O_3 (0.5 wt. % Pd) with Stirring.

Temperature, °C.	Duration, hr	Amount of Palladium Recovered, g	Degree of Recovery of Palladium, %
	Palladium-aluminosilicate		
20	1	0,2666	79,8
20	1	0,3250	87,0
20	3	0,356	93,6
20	5	0,3598	95,5
40—50	3	0,3598	95,5
	Palladium-aluminum oxide		
20	3	0,2173	86,9
40—50	3	0,2[illegible]	98,6

In the electrochemical reduction of palladium from its chloride and nitrate solutions, the deposition rate is proportional to the total concentration of the solution, is independent of the pH of the medium, but is limited by the rate of diffusion of the ions to the electrode surface [287]. This factor determines the magnitude of the limiting current of deposition of palladium [296]. The deposition of palladium from an alkaline solution is associated with passivation of the palladium electrode [297].

Of interest is a study [298] of the separation of precious metals from solutions of their salts by means of ion exchange resins. Data are available on the quantitative absorption of platinum, palladium, rhodium, and iridium in the form of chloride complexes (anions). To separate the platinum group metals (after their absorption on a cation exchange resin from a salt solution containing no halogens), platinum should be washed with water, palladium with 0.05-5.0 M hydrochloric acid, rhodium with 2 M hydrochloric acid, and iridium with 4 M hydrochloric acid. Studies have been made on the chromatographic separation of platinum group metals from copper, iron, and nickel on the KU-I cation exchange resin.

Role of the Carrier

While the method of preparation of low-percentage catalysts determines their dispersity and amount of specific surface, the chemical nature of the carrier and structure of its pores have a decisive influence on the efficiency, stability, quantity and structure of the active centers of contacts [303, 304, 305].

The porosity of contacts is of major importance in their practical applications. The maximum utilization of the volume of the grain in the case of reactions taking place at low pressures is achieved by using heterogeneous structures with large pores (bidisperse carriers), and at high pressures, homogeneous fine-pored structures [190, 305].

For low-percentage oxidation catalysts frequently operating under diffusion conditions, the best-suited may be structures with wide pores on the surface of which the active substance deposits. With such a structure of the carrier pores, the active phase is utilized to the maximum extent.

The study [54] compares low-percentage platinum, palladium, and platinum-palladium catalysts on a number of carriers in the oxidation reaction of carbon monoxide. As is evident from the results, the nature of the carrier substantially affects the degree of oxidation of CO, particularly at low temperatures (200-250°C.).

The influence of the carrier is clearly manifested when one analyzes the specific oxidation rate constants of CO, obtained by referring the rate constant (calculated from the first-order equation $K = \frac{23}{\tau} \cdot \frac{1}{1-\alpha}$ or degree of conversion) to 1 g of metal. Tables 15 and 16 list the values of the specific rate constants for oxidation of carbon monoxide on palladium and platinum catalysts obtained by our proposed method. The specific activity in the series of palladium and platinum catalysts on different carriers decreases by one order of magnitude from aluminum oxide to ceramics and the insulating material (Fig. 20, 21, 22). Attention is drawn to the relatively high activity of contacts on carriers whose composition contains γ-Al_2O_3 (aluminosilicate, Houdry contact, molecular sieve). A similar pattern but not as clearly manifested is observed in the case of platinum contacts

Table 15

Specific Activity of Palladium Catalysts on Carriers (0.5 wt. %) in the Oxidation Reaction of 1% CO in a Stream of Air at $V = 36 \times 10^3$ hr^{-1}

Carrier	% Conversion of CO		Weight of Catalyst, g	Amount of Pd, g x 10^{-3}	$K^{200°C}$, sec^{-1}	Specific Activity of 200°C. on 1 g of Pd	
	200°	250°				% Conversion on 1 g of Pd	K_{sp} x 10^3
Aluminum oxide, A-1	90	100	1,18	5,90	37,1	15,2	6,56
ShAS-2 bead aluminosilicate	60	100	1,32	6,60	14,7	9,1	2,23
Houdry contact	54	80	1,07	5,35	11,7	10,0	2,19
Molecular sieve	61	100	1,68	8,4	15,1	7,2	1,79
ShSK silica gel	41	66	1,02	5,1	8,5	8,0	1,67
Foam glass	26	50	1,03	5,15	4,8	5,0	0,94
Keles clay	42	95	2,14	10,7	8,7	3,9	0,81
Insulating material	29	93	2,30	11,5	5,4	2,5	0,46
Ceramic	19	66	2,30	11,5	3,3	1,6	0,29

Table 16

Specific Activity of Platinum Catalysts, on Carriers (0.5 wt. %) and Activated at 500°C. in a Stream of Air, in the Oxidation Reaction of 1% CO in a Stream of Air at $V + 36 \times 10^3$ hr^{-1}

Carrier	% Conversion of CO at 200°C.	Weight of Catalyst, g	Amount of Platinum, g x 10^{-3}	$K^{200°C.}$, sec^{-1}	$K_{sp}^{200°C.}$ x 10^3
A-1 aluminum oxide	100	1,226	6,1	74,2	12,3
Houdry contact	97	1,405	7,0	56,48	8,06
Molecular sieve	93	1,736	8,9	63,03	7,0
Silica gel	90	1,027	5,1	37,1	6,2
Baku ShAS	87	1,534	7,69	32,9	4,2
Foam glass	65	0,96	4,8	16,8	3,5
Ceramic	70	2,07	10,35	19,38	1,8

obtained by impregnation followed by brazing with an organic paste, when less favorable conditions exist for the precipitation of fine platinum crystals on the surface and for their interaction with the support (Table 17).

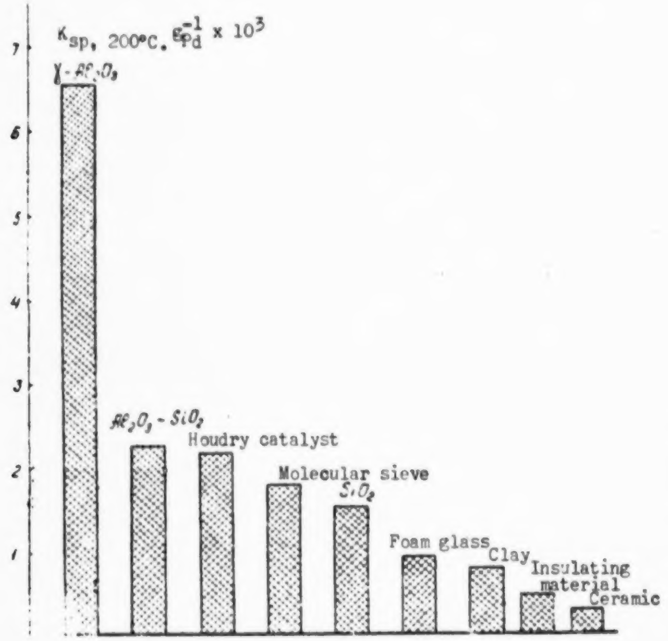


Fig. 20. Specific activity of supported palladium catalysts in the oxidation reaction of carbon monoxide (0.5 wt. % of metal).

The same effect of γ-Al_2O_3 as carrier was observed in the oxidation reaction of CO on copper-chromium contacts (Table 18).

The increase in the specific activity of copper-chromium catalysts on γ-Al_2O_3 is explained in [396] by the stabilization of the copper ion in the defect structure of aluminum oxide, as expressed in a weak EPR signal (unsymmetric singlet, g-factor close to 2.05-2.09). The strength of the EPR signal shows a considerable increase of the electron density in the system, favoring a donor-acceptor mechanism of the reaction.

The high activity of copper and chromium catalysts deposited on γ-Al_2O_3 and MgO carriers in dehydrogenation reactions of cyclohexane and cyclahexanol was reported by B. V. Yerofeyev et al. [393]. The authors attribute this to the fact that the structure of these carriers contains octahedral cationic sites at which the deposited metals are stabilized.

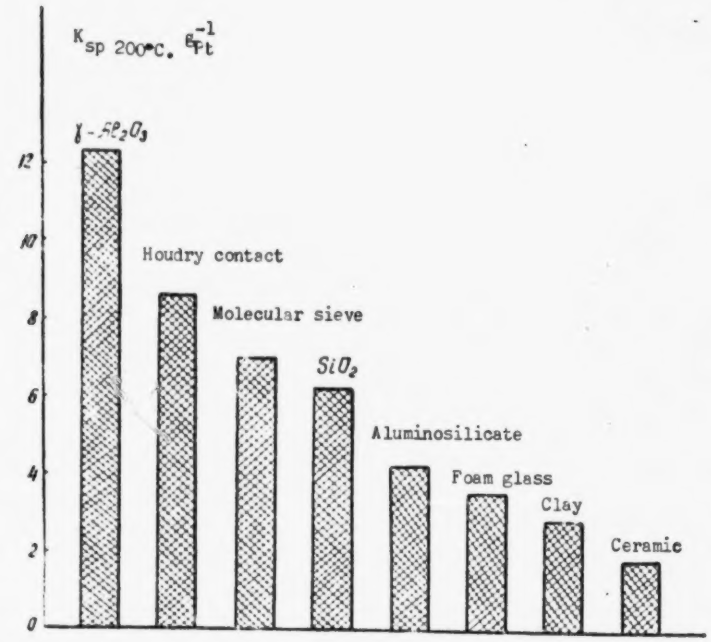


Fig. 21. Specific activity of supported platinum catalysts in the oxidation reaction of carbon monoxide (0.5 wt. % of metal).

Table 17

Specific Activity of Supported Platinum Catalysts (0.5 wt. % Pt), Prepared by Brazing from an Organic Paste, in the Oxidation Reaction of 1% Carbon Monoxide in a Stream of Air at V = 36 x 10^3 hr^{-1} abd 200°C.

Carrier	% Conversion of CO	Weight of Catalyst, g	Amount of Platinum, g x 10^{-3}	$k^{200°C}$, sec^{-1}	Specific Activity at 200°C. on 1 g of Pt	
					% Conversion on 1 g of Pt	K_{sp} x 10^3
A-1 aluminum oxide	90	1,3	7,01	37,1	12,8	5,29
Houdry contact	84	1,40	7,0	29,5	12,0	4,21
Porcelain	96	2,77	13,8	51,8	6,95	3,76
ShAS-2 bead aluminosilicate	79	1,4	7,0	25,6	11,3	3,65
Keles clay	80	2,2	11,0	25,9	7,27	2,35
Corundum	77	3,33	16,9	23,5	4,55	1,39

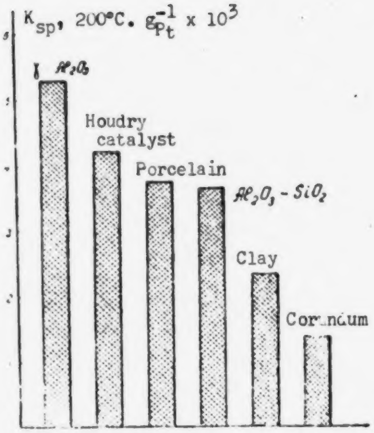


Fig. 22. Specific activity of supported platinum catalysts (0.5 wt. % of metal), obtained by brazing from an organic paste, in the oxidation reaction of carbon monoxide.

Maxted [426] pointed out that the reaction rate for the hydrogenation of cyclohexene on platinum and palladium depends on the nature of the carrier. Calculation of the specific activity (amount of hydrogen absorbed at the fourth minute on 1 g of active metal) for 1% palladium catalyst, based on the data of the study, indicates that this activity decreases in the following order: Cr_2O_3 (25-27 x 10^3), Al_2O_3 (20 x 10^3), TiO_2 (18 x 10^3), ThO_2 (12 x 10^3), MgO (9 x 10^3), ZrO_2 (4 x 10^3), and V_2O_5 (3 x 10^3).

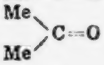
The special properties of γ-Al_2O_3 as a carrier in the oxidation reaction of carbon monoxide become clear when one examines the adsorptive properties and reactivity of the deposited metals for different degrees of surface coverage. The character of the IR spectra of carbon monoxide adsorbed on rhodium, ruthenium, platinum, and palladium depends not only on the nature of the metal, but also on the carrier [421]. A study of the adsorption of carbon monoxide

Table 18

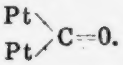
Effect of the Carrier on the Oxidation of 1% CO in a Stream of Air on Copper-Chromium Catalysts [395].

Carrier	Color of Catalyst	Degree of Oxidation of CO, %				$K^{300°C.}$, sec^{-1}	$K^{300°}$ $\frac{1}{\text{g of Active Phase}}$	EPR Signal	
		200°	300°	400°	500°			Form	g
Corundum	Black	—	35	58	80	10	68	Narrow signal	1,97
Clay	Dark green	22	26	30	45	6	33	Broad symmetric singlet	2,0
Alumino-silicate	Black	12	41	64	80	10	84	Unsymmetric singlet	2,09
γ-Al_2O_3	Light green	41	93	99	100	52	443		
γ-Al_2O_3 after 42 hours of use		42	89	100	100	42	362	•	—
Cu/γ-Al_2O_3	Light green	10	62	99	100	23	390	•	2,05

on platinum and palladium catalysts on charcoal reveals the predominance of the linear structure of carbon monoxide [382].

Adsorption State	ml CO/g Pt	ml CO/g Pd
Me=C=O	115	211
	57,5	105,5

Whereas in the adsorption of carbon monoxide on platinum on silica gel and on a platinum film a linear structure also predominates (there is a strong band in the spectrum at 4.8 μ), and approximately 15% of CO is adsorbed in the form of a bridge structure (absorption band at 5.3 μ), in the case of Pt/Al_2O_3 as many as 50% of the CO molecules are bound to the surface in the form of bridge structures (cf. Fig. 23) [344, 345, 383, 384]



As is evident from Fig. 23, the absorption band corresponding to the linear structure of CO shifts to 4.9 μ. It is highly probable that the bridge structure of carbon monoxide is more reactive in the reaction of its oxidation.

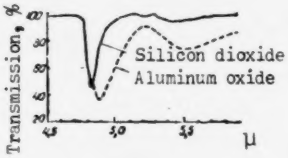


Fig. 23. Spectra of carbon monoxide chemisorbed on platinum on silica gel and aluminum oxide [345].

Kral [382] studied the chemisorption of carbon monoxide on low-percentage platinum and palladium catalysts on γ-Al_2O_3. Three varieties of aluminum oxide were selected: bayerite, boehmite, and boehmite gel. It was found that the impregnation method affects the distribution of the metal in low-percentage catalysts and its specific surface. Impregnation of aluminum hydroxide followed by calcination at 500°C. and reduction in hydrogen at 200°C. allows a larger surface and a better distribution of the precious metal than when the impregnation with chloroplatinic acid solution is carried out after calcination of aluminum oxide.

The author showed that the chemisorption of carbon monoxide increases with decreasing amount of metal deposited on the carrier (Fig. 24). Maximum adsorption is observed when bayerite is used as the carrier. Calculation of the ratio of the number of CO molecules to the number of metal atoms, which we carried out by using Kral's data, showed that this ratio increases in the range of low degrees of coverage; for the 1% platinum catalyst it approaches 1.7, and for the 1% palladium catalyst it also exceeds unity (1.14). If the calculation allows for the fact that part of the carbon monoxide molecules are adsorbed on platinum and palladium on γ-Al_2O_3 in the form of bridge structures, the ratio obtained will increase even more.

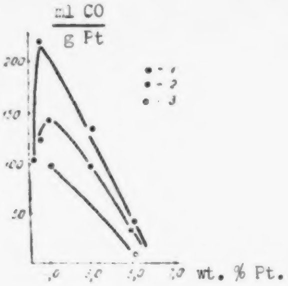


Fig. 24. Adsorption of carbon monoxide on platinum catalysts on varieties of aluminum oxide as the platinum concentration changes [382]. 1 - Bayerite; 2 - Boehmite gel; 3 - Boehmite.

The data obtained by Kral attest to the excess adsorption of carbon monoxide on platinum and palladium on γ-Al_2O_3 in the range of low coverages.

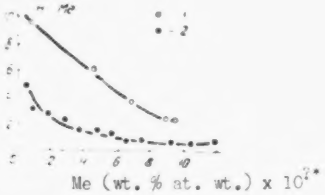


Fig. 25. Number of hydrogen atoms per atom of metal as a function of the metal content on the carrier [307]. 1 - Pd/Al_2O_3; 2 - Pt/Al_2O_3.

The high adsorptive capacity of platinum and palladium catalysts on γ-Al_2O_3 for hydrogen was observed earlier by D. V. Sokol'skiy and Ye. I. Gil'debrand [306, 307, 309]. It was shown that in the range of small coverages, the number of hydrogen atoms per metal atom is 10 for platinum and 5 for palladium (Fig. 25). Similar results were obtained in the 1930's by A. N. Frumkin for platinum on charcoal [336, 419].

D. V. Sokol'skiy explains the observed effect by the peculiar state of the carrier surface at a considerable distance from the center of atomization of the hydrogen molecule, the transfer of hydrogen atoms to the adsorption center, and diffusion of molecular hydrogen on the surface from the adsorption centers to the centers where dissociation of the hydrogen molecules takes place [232].

A larger-than-stoichiometric increase in the adsorptive capacity of platinum on Al_2O_3 for hydrogen was also observed by Adler, Spenadel and

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* Editor's note: Illegible broken type.

Boudart [352, 422]. The ratio of hydrogen atoms to platinum atoms for 0.1-0.3% platinum was 1.44, and for 0.8%, 1.65. The authors explain this fact by an increase in the dispersity of the metal crystals on the carrier. According to their calculations and x-ray data, the size of elementary platinum crystals in the range of high hydrogen adsorption approaches the size of individual atoms (10-12 Å) possessing an extended surface which, however, turned out to be greater than that which can be occupied by the amount of platinum taken. Hence it is concluded that a certain amount of hydrogen is adsorbed between the platinum particles. The latest studies confirm D. K. Bond's theoretical calculation [427] of the increase in the fraction of single surface atoms of metals (on the edges and peaks of crystals) with increasing dispersity of crystals of group 8 metals, which form a euboctahedron. Bond showed that the special catalytic and adsorptive properties of very fine crystals are related to the properties of atoms having low coordination numbers.

Table 19

Oxidation of 1% CO in a Stream of Air on 3.53 g of Platinum and Palladium Catalysts on Aluminum Oxide (ShN-2, Particle Size 0.1-0.2 mm) With Different Contents of Metals at $V = 36 \times 10^3$ hr^{-1}

% Me	Pd Content, g x 10^{-3}	% Conversion CO		K, sec^{-1}		K_{sp}, $\frac{\text{sec}^{-1}}{\text{g Pd}} \cdot 10^3$		log $K_{sp} \times 10^3$	
		150°	200°	150°	200°	150°	200°	150°	200°
0,1 Pd	3,53	12	70	1,85	19,38	0,525	5,49	2,7160	3,7336
0.2	7,06	23	88	3,77	34,16	0,533	4,83	2,7267	3,6839
0.25	9,07	25	89	4,16	37,1	0,458	4,039	2,6609	3,6117
0.35	12,7	27	90	4,55	37,1	0,358	2,92	2,5539	3,4654
0,5	17,6	30	92	5,15	40,69	0,292	2,31	2,4654	3,3636
0,1 Pt	3,53	17,5	33	2,77	6,44	0,786	1,827	2,8954	3,2617
0.2	7,06	23	70	3,77	19,3	0,533	2,75	2,7267	3,4393
0,25	9,07	24	71	3,95	19,9	0,436	2,198	2,6395	3,342
0,35	12,7	26	75	4,34	22,34	0,342	1,76	2,5340	3,2452
0,5	17,6	26	80	4,34	25,93	0,247	1,473	2,3927	3,1682

An increase in the adsorptive capacity of low-percentage platinum and palladium catalysts on γ-Al_2O_3 for gases (hydrogen, carbon monoxide) whose adsorption proceeds via an electron-donor mechanism increases the specific catalytic activity in reactions whose rate-determining step is the activation of hydrogen and carbon monoxide. The beneficial effect of γ-Al_2O_3 as a carrier in dilute layers was manifested in a series of reactions: exchange of hydrogen on deuterium [414], oxidation of sulfur dioxide [338, 340] and ammonia [418], dehydrogenation of cyclohexane [337] and hydrogenation of ethylene and its homologs [339, 415]. Analysis of the reactivity of metal catalysts by means of the theory of active ensembles established that the active center in these processes, which occur on low-percentage platinum and palladium contacts on aluminum oxide, aluminosilicate, and charcoal, is a monatomic ensemble which "is formed on particularly active areas of the carrier" and forms a "mixed ensemble" from atoms of platinum and of the active center of the carrier [339].

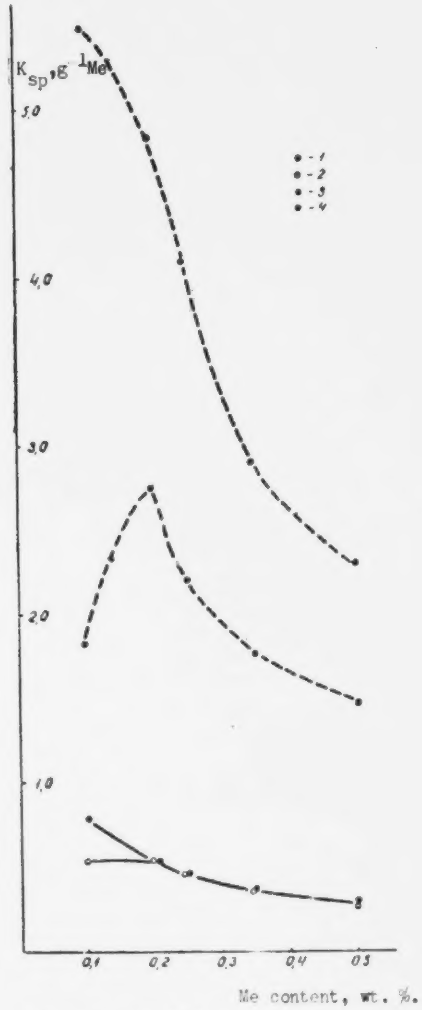


Fig. 26. Specific activity of palladium (1, 2) and platinum (3, 4) catalysts on γ-aluminum oxide in the oxidation reaction of carbon monoxide in a stream of air at a space velocity of 36 x 10^3 hr^{-1} at 150°C. (solid line) and 200°C. (dashed line).

Zh. V. Strel'nikova and V. P. Lebedev [341, 342] proposed a mechanism for the catalytic action of such active centers in hydrogenation reactions, allowing for the possibility of dissociative adsorption of the reacting atoms and molecules on a divalent monatomic active center followed by diffusion to the active centers of the carrier.

Our calculation of the specific activity of platinum and palladium on γ-aluminum oxide in the osication reaction of carbon monoxide, carried out (see Table 19 and Fig. 26) in the range of 0.1-0.5% content of the metals, showed that as the metal content on the carrier decreases, the specific activity increases.

The rectilinear form of the dependence of log K_{sp} on the degree of coverage of the carrier surface by platinum or palladium (the metal content in wt. % was taken as α) demonstrates (Fig. 27) that the oxidation reaction of carbon monoxide proceeds at a metal content below 0.5% on single atoms of platinum and palladium sparsely distributed over the carrier.

Something different is observed in the case of palladium catalysts on synthetic aluminosilicate with a high metal content (ShAS-2, particle size 4 mm). As the total activity increases with the palladium content rising from 0.1 to 1.0%, a minimum at 0.3% Pd and a maximum at 0.75% Pd appear in the variation of the specific activity. We were unable to calculate the number of atoms n in the composition of the active center up to 0.3% Pd because of the limited number of points; at a Pd content above 0.3%, this number is equal to two, as indicated by the rectilinear form of the dependence of log K_{sp}/% Pd (Fig. 28) on the palladium content of the catalysts. A similar effect was noted by N. I. Kobozev et al. [417, 339] in a study of platinum catalysts on oxides of magnesium and chromium and on silica gel in hydrogenation reactions of cyclohexene and ethylene and decomposition of hydrogen peroxide. It was shown that at a high platinum content (second maximum), new active centers are formed (n = 2) whose structure differs from the composition of the structure correspodning to low coverages (n = 1).

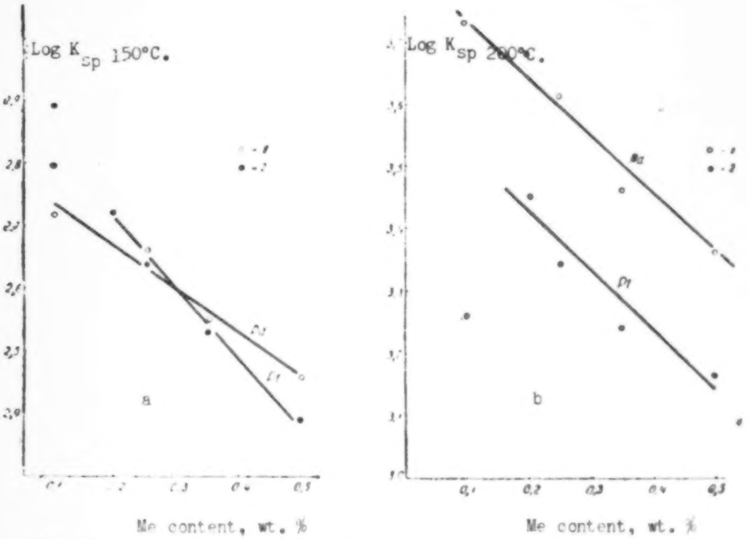


Fig. 27. Log of the specific rate constant of the oxidation reaction of carbon monoxide vs. metal content in Pd (1) and Pt (2) catalysts on γ-aluminum oxide: a - at 150°C., b - at 200°C.

A comparison of the adsorptive properties with respect to carbon monoxide [382] and catalytic properties of low percentage platinum and palladium catalysts on γ-Al_2O_3 in the oxidation reaction of 1% carbon monoxide in a stream of air revealed a certain parallelism. The latter is expressed in a substantial increase of the specific adsorption of carbon monoxide and catalytic activity in the range of low content of the active metals (0.1-0.2 wt. %). The observed relationship between the adsorptive and catalytic properties is due to the mechanism of the oxidation reaction of carbon monoxide; when this reaction is carried out in excess oxygen, its rate is limited by the activation of carbon monoxide. The activation of carbon monoxide improves on metals deposited on aluminum oxide, which is capable of adsorbing carbon monoxide on the surface [343] and exerting an influence on the predominant adsorption of carbon monoxide in the form of a bridge structure on low-percentage metal catalysts.

The remarkable adsorptive properties of low-percentage platinum and palladium catalysts on γ-Al_2O_3 and the mechanism of action of monatomic active

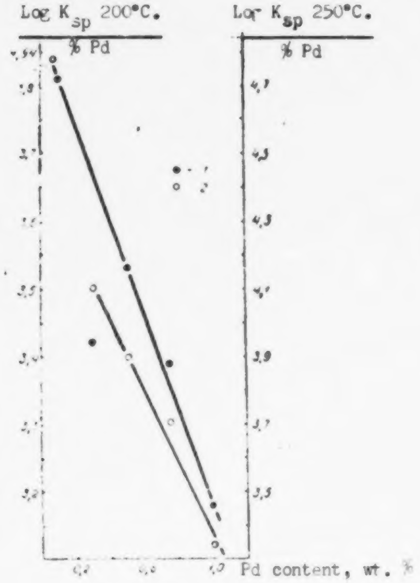
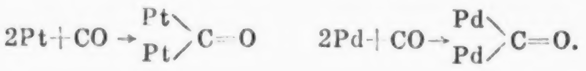


Fig. 28. Log K_{sp}/% Pd vs. palladium content on aluminum oxide in the oxidation reaction of carbon monoxide. 1 - 200°C.; 2 - 250°C.

centers in the oxidation reaction of CO can be explained, as in hydrogenation processes, only by assuming the participation of the carrier in the catalytic event.

Apparently, the adsorption and activation of carbon monoxide, as in the case of hydrogen [341, 342], occurs in two steps. In the first step, carbon monoxide is chemisorbed on the monatomic divalent metal centers of low-percentage catalysts, with the formation of a bridge structure and a linear structure

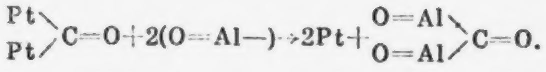
$$\text{I. } Pt + CO \rightarrow Pt{=}C{=}O \qquad Pd + CO \rightarrow Pd{=}C{=}O$$



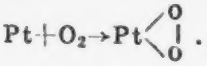
$$2Pt + CO \rightarrow \begin{matrix} Pt\diagdown \\ Pt\diagup \end{matrix}C{=}O \qquad 2Pd + CO \rightarrow \begin{matrix} Pd\diagdown \\ Pd\diagup \end{matrix}C{=}O.$$

This process of donor-acceptor interaction takes place at a high rate because of the tendency of the elements with an unfilled d subshell to bring the number of outer electrons up to 18 by acquiring two electrons of carbon monoxide [425].

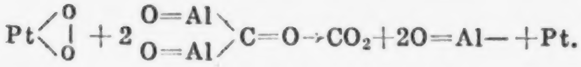
The second stage involves diffusion of carbon monoxide from the metal centers to the active centers of the carrier, and as a result, the monatomic platinum and palladium centers become free and able to activate oxygen and fresh amounts of carbon monoxide.

II. 

$$\begin{matrix}\mathrm{Pt}\diagdown\\ \mathrm{Pt}\diagup\end{matrix}\mathrm{C{=}O}+2(\mathrm{O{=}Al{-}})\rightarrow 2\mathrm{Pt}+\begin{matrix}\mathrm{O{=}Al}\diagdown\\ \mathrm{O{=}Al}\diagup\end{matrix}\mathrm{C{=}O}.$$

III. 

$$\mathrm{Pt}+\mathrm{O_2}\rightarrow\mathrm{Pt}\begin{matrix}\diagup\mathrm{O}\\ \quad|\\ \diagdown\mathrm{O}\end{matrix}.$$

IV. 

$$\mathrm{Pt}\begin{matrix}\diagup\mathrm{O}\\ \quad|\\ \diagdown\mathrm{O}\end{matrix}+2\begin{matrix}\mathrm{O{=}Al}\diagdown\\ \mathrm{O{=}Al}\diagup\end{matrix}\mathrm{C{=}O}\rightarrow\mathrm{CO_2}+2\mathrm{O{=}Al{-}}+\mathrm{Pt}.$$

The active centers of the carrier in the case of γ-Al_2O_3, whose face-centered crystal lattice constitutes a defect spinel with a deficiency of cations [325, 326] at octa- and tetrahedral interstitial sites, are aluminum atoms (Fig. 29) [393]. The latter occupy a part of the octahedral interstitial sites of γ-Al_2O_3 and have a tendency to fill the incomplete 3p subshell with electron pairs [327]. The ability of the aluminum atom to enter into a donor-acceptor interaction with adsorbed atoms and molecules in the role of an electron acceptor is indicated by IR spectroscopic data [327, 428, 429].

This property was confirmed by an EPR study of the adsorption of quinones on γ-Al_2O_3 [412]. It was shown that when the calcination temperature is raised from 100 to 400°C., the relative number of adsorbed radicals becomes 5 times greater as a result of an increase in the number of electron-acceptor centers. An increase in the concentration of electron-acceptor centers in γ-Al_2O_3 as the calcination temperature is raised to 900°C. is also indicated in [428].

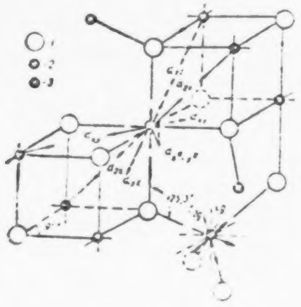


Fig. 29. Octahedral and tetrahedral sites of atoms in spinel structures. Arrows indicate the orientation of d orbitals: 1 - oxygen atom; 2 - tetrahedral sites; 3 - octahedral sites of atoms [393].

On the surface of aluminosilicates, in addition to electron acceptor centers, there are proton-donor centers whose proportion and number are determined by the content of aluminum and silicon oxides and their calcination temperature [327, 428, 430].

The deficiency of electrons in the structure of γ-Al_2O_3 accounts for its slight semiconducting properties (p-type), manifested at a relatively low temperature and upon deposition of 1-10% platinum [324].

The imperfection of the structure of γ-Al_2O_3 and the presence of electron-acceptor centers account for its capacity to adsorb CO and hydrogen. The amount of the latter is slight (~0.15-1 ml/m^2) and increases during heat treatment, especially above 400°C. [329-331] and in the presence of transition metal impurities [333, 387]. Metal atoms on the surface of γ-Al_2O_3 substantially accelerate the adsorption process [415].

It is possible that the adsorption of carbon monoxide takes place directly on the surface of γ-Al_2O_3, with migration of adsorbed molecules to centers with a high binding energy [328]. Such centers may be electron-acceptor areas of γ-Al_2O_3 and also atoms or ions of adsorbed metals Pt, Pd [315, 317], Cr [334], or Cu [393].

Owing to the adsorption, for example of hydrogen, on Al_2O_3 (in some cases added to the catalyst in the form of a mechanical mixture [416, 420]) and diffusion to the platinum centers, there is an increase in the rate of reduction of compounds whose hydrogenation has the activation of hydrogen as its rate-limiting step.

Thus, in the case of low-percentage metal catalysts, the peculiar structure of γ-Al_2O_3 is conducive to involvement in the catalysis of an extensive area of the carrier (up to 10 active centers of the carrier) accessible to the surface diffusion of the reactants.

The ability of γ-Al_2O_3 to form reserves of molecular and chemisorbed forms of electron-donor molecules and atoms (carbon monoxide, hydrogen) on their surface and also to exert a decisive influence on the form and energy of the bonding of adsorbed atoms (bridge and linear structures of carbon monoxide) and on the structure of the active center causes an increase by one order of magnitude or more in the specific activity of platinum, palladium and other metal catalysts on γ-Al_2O_3 in oxidation, reduction, and dehydrogenation reactions.

A necessary condition for the manifestation of the specific properties of γ-Al_2O_3 is its extensive interaction with isolated atoms of deposited metals. This interaction consists in the penetration of the metal atoms into the crystal lattice of the carrier, in which there is a deficiency of cations at octa- and tetrahedral interstial sites. Calculations of the stabilization energy of atoms carried out by B. V. Yerofeyev et al., based on the ligand field theory for chromium and molybdenum catalysts on γ-Al_2O_3, showed that the principal sites of metal stabilization are octahedral vacancies frequently occupied by aluminum atoms. "Octahedral vacancies may contain atoms or ions of chromium, molybdenum, or other metals" [393]. When a transition metal ion or atom enters the carrier lattice in an octa- or tetrahedral ligand field, the d electron orbitals are split into two groups: three t2g orbitals and two te orbitals [392, 393].

The electronic nature of the interaction of the deposited metals with the carrier is indicated by experimental data obtained by studying the deposited catalysts by methods of exoelectron emission, resonance, and magnetic susceptibility [319, 320, 321, 334, 339]. N. I. Kobozev et al. [320] noted that the atomization of deposited metals in the range of small coverages causes the phenomenon of superparamagnetism. The relative magnetization increases with decreasing degree of coverage and is determined by the nature of the metal and carrier (Fig. 30). An increase in magnetic susceptibility at relatively low concentrations of oxides of nickel, chromium, manganese, iron, and copper on the carriers was observed by Selwood [319]. He explained this effect by a change in the valence state of the adsorbed ions.

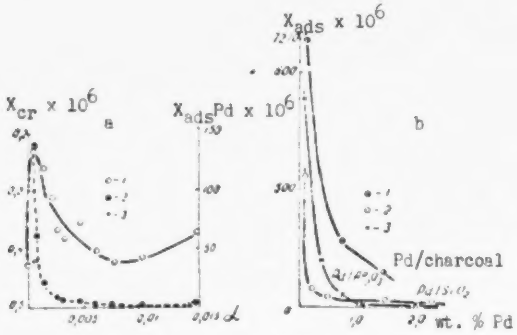


Fig. 30. Magnetic susceptibility of supported platinum catalysts on silica gel (a) and palladium catalysts (b) after the data of Strel'nikova, Lebedev, Pospelova, and Tshebyatovskiy (for palladium) 320.
1 - Palladium on charcoal; 2 - palladium on aluminum oxide; 3 - palladium on silica gel

N. I. Kobozev et al. also explained this phenomenon by electronic transitions between the adsorbed metal atoms and the carrier. "This phenomenon is due to electronic processes in the energy bands of the carrier, since the effect of superparamagnetism is influenced not only by the degree of dilution, but also by the nature of the substance deposited and of the carrier. The paramagnetic susceptibility of platinum adsorbed on silica gel varies widely with the brand of silica gel from 140 x 10^{-6} to 566 x 10^{-6} units" [320]. In palladium, the susceptibility is higher than in platinum and depends on the nature of the carrier: Pd/WO_3 - 12.5 x 10^{-6}; Pd/SiO_2 - 510 x 10^{-6}; Pd/Al_2O_3 - 580 x 10^{-6}; Pd/charcoal - 7200 x 10^{-6} (Fig. 30). Kobozev explains the high paramagnetic susceptibility of palladium by postulating an easy transition of an electron from the $4d^{10}$ subshell to the 5S subshell (0.8 eV).

The pulling off of the outer electrons of the deposited metals by the carrier is also indicated by data obtained by Nikolau and Thom [321]. By studying the resonance of metallic platinum and palladium on charcoal

(1-5 wt. %), they showed that the metal is stabilized between the aromatic rings of the graphite lattice with the formation of pseudo-sandwich structures in which a highly delocalized electron is supplied by the platinum.

Upon splitting of the 4 d levels of palladium and transition of an electron to the 5S subshell, the structure of its outermost electron shell becomes similar to that of platinum. As a result of interaction with the carrier, the palladium atom loses many properties characteristic of the massive metal. The "platinumlike" nature of palladium in the range of low concentrations is manifested in its adsorptive, electrochemical and catalytic properties [306-316]. These properties are expressed in a lack of ability to dissolve hydrogen upon adsorption (the α-β transition portion of the charging curves disappears), and in the form of the kinetic curves of hydrogenation of acetylenic compounds (similar to the curves for the platinum contact).

Starting at some minimum palladium concentrations, individual atoms may cluster during surface migration and pass to the crystalline state [318], this being dependent on both the quantity of the metal and the nature and structure of the carrier. The crystallization of palladium, for example, on powdered barium and calcium sulfates takes place at 0.1-0.2%, on silica gel at 0.4-0.5% palladium, and on charcoal, at a 0.6-0.7% metal content [315, 316]. A precise method of determining the degree of crystallization and properties of palladium on a carrier may be catalytic hydrogenation [317].

The "platinumlike" nature of the low-percentage catalyst is also displayed in the reaction of catalytic oxidation of carbon monoxide. It has been noted that the activity of palladium on the γ-Al_2O_3 carrier in the range of content of active components below 0.5 wt. %, when the carrier takes an active part in the reaction, is equal to or higher than the activity of the platinum catalyst (cf. Fig. 26). At a metal concentration of 0.5 wt. % and above, when diatomic and more complex ensembles are responsible for the catalysis, for a similar percent oxidation of carbon monoxide, the specific activity of platinum on most carriers (cf. Table 15, 16) becomes higher than that of palladium catalyst. At the same time, the influence of the chemical nature and structure of the carrier on the specific activity of the catalysts is manifested to a lesser degree.

The method of preparation of low-percentage catalysts has a decisive influence on the process of formation of the active centers of metal catalysts (cf. Tables 16 and 17). When the catalysts are prepared by our method, there takes place a rapid reduction of palladium or platinum from the complexes at a low temperature and the formation of fine imperfect crystals of irregular shape with a high content of the atomic phase. Conditions are thus created for an atomic distribution of the metal (at a palladium concentration of less than 0.5 wt. %) over the surface and for chemical interaction with carriers containing active aluminum oxide.

When catalysts are obtained by impregnation with a viscous organic mixture followed by reduction of the metals by calcination at a high temperature, coarse metal crystals are formed whose interaction with the carrier is difficult. In this method of preparation, the influence of the nature of the carrier is less pronounced.

The high catalytic activity of the palladium catalyst in the oxidation reaction of carbon monoxide, comparable to that of platinum, made it possible to recommend it for the removal of carbon monoxide and other toxic components from motor transport exhausts and other oxygen-containing gas mixtures and as a substitute for the more expensive and scarce platinum catalyst.

Thus, owing to its crystallographic structure, the carrier in low-percentage catalysts can fulfill a number of functions important in catalysis:

1. Change the nature of deposited metals by stabilizing them chemically at the vacant sites of a defect structure, for example, in γ-Al_2O_3.

2. Facilitate the course of the rate-determining steps by participating in the adsorption and activation of the reacting molecules and thus accelerate certain reactions, for example, the donor-acceptor interaction in the case of γ-Al_2O_3. The most active carriers for oxidation, hydrogenation and dehydrogenation catalysts are aluminum oxide and other compounds of spinel structure in which electronic transitions between ions in tetra- and octahedral interstitial sites take place without any appreciable consumption of energy [450].

3, In the case of reactions involving the formation of intermediates, the role of the carrier is manifested in still another way. Because of the possibility of surface migration of the initial, final and intermediate reaction products on the carrier, a directing function of the carrier is observed, so that in some cases the processes occur at high rates and in a strictly selective manner [299, 346-348, 388].

Stability, Structure and Phase Composition of Catalysts in Prolonged Use

One of the chief requirements for catalysts to be used in the purification of exhausts of internal combustion engines is a high chemical and thermal stability. In bench and road tests under service conditions, the catalyst is subjected to the action of the reaction mixture and overheatings whose character depends on the type of engine and its load, the technical condition of the automobile, its mode of operation, and the design of the gas purifier. The content in the exhaust gas of carbon monoxide, hydrocarbons, and aldehydes, whose oxidation is associated with the liberation of large amounts of heat, may vary over wide limits. At high traveling speeds of automobiles (60-100 km/hr) with carburetor engines, during idling and braking, the carbon monoxide content of the exhaust gas increases sharply and may reach 10-12%. This causes the catalyst to heat up considerably, to 800-900°C. In the course of operation in the stream of diesel engine exhausts, the catalyst operates in excess O_2 (20-21%).

To determine their stability, low-percentage catalysts were subjected to a prolonged heat treatment in a stream of air, were artificially overheated, and the possibility of increasing their activity after decreasing it was studied [61].

Table 20

Stability of Low-Percentage (0.5 wt. % Metal) Catalysts on Keles Clay.

Catalyst	Calcination of Catalyst		Degree of Oxidation of CO, %		
	Time, hr	Temperature, °C.	200°	250°	300°
Platinum	2,0	500	84	100	100
	26,0	500	75	100	100
Platinum-Palladium	2,0	400	80	100	100
	26,5	400	50	90	100
Palladium	2,0	400	95	100	100
	27,5	400	65	92	100

The heat treatment of low-percentage catalysts with air (for up to 27 hours at 400-500°C.) has little effect on their activities in the oxidation reaction of CO (Table 20). At 300°C. and above, carbon monoxide is completely oxidized. At lower temperatures, a certain decrease of the degree of oxidation is observed which is maximum (30% at 200°C.) in the case of palladium.

The activity of platinum catalyst (0.5 wt. % Pt) on bead aluminosilicate in the course of oxidation of carbon monoxide in a mixture with air at 500°C. also showed practically no decrease (after being tested for 32 hours). At 250-500°C., carbon monoxide was completely oxidized, and at 200°C. the degree of oxidation ranged from 90 to 100%. Raising the service temperature of the catalyst to 600°C. did not decrease the degree of oxidation of carbon monoxide either.

The platinum-palladium catalyst on bead aluminosilicate was tested during a gradual increase of the oxidation temperature to 700°C. The results (Fig. 31) showed that its activity (which at 200-250°C. is less than that of the platinum catalyst) is preserved for a long time (170 hours) at 400-650°C. Oxidation of 1% carbon monoxide mixed with air at 650°C. slightly raises the degree of oxidation of carbon monoxide at 200-250°C., which again decreases starting at 700°C.

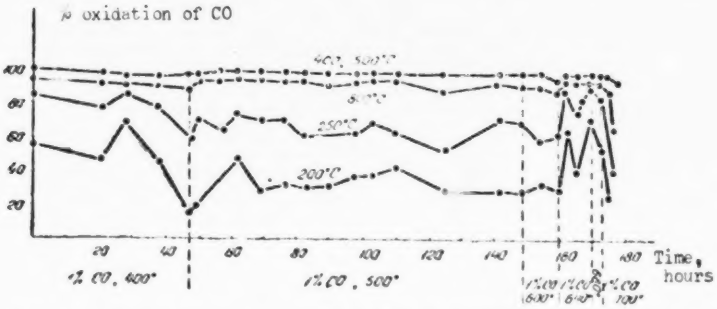


Fig. 31. Effect of temperature and time of treatment of platinum-palladium catalyst on aluminosilicate with a mixture of 1% carbon monoxide and air on the activity in the oxidation reaction of 1% CO at lower temperatures.

Like platinum contact, palladium catalyst on bead aluminosilicate after a 40-hour oxidation of carbon monoxide (1%) and a gradual temperature elevation to 600°C. oxidizes carbon monoxide completely at 250°C. and above. At 200°C., the activity of palladium catalyst is 30% lower than that of platinum catalyst, but does not decrease, and even increases (up to 82%) during prolonged use, particularly for 6 hours at 600°C. Thus, the heat treatment of low-percentage platinum, palladium and platinum-palladium catalysts in a stream of air and during the oxidation of carbon monoxide at temperatures up to 600-650°C. practically does not decrease their activity. This indicates a high thermal stability of the catalyst at these temperatures.

The results obtained are a consequence of a property characteristic of low-percentage catalysts: as the temperature is raised to 600-650°C., no coarsening of the crystals is observed, and only their defects are eliminated. This property has been noted by many researchers [385, 422]. Thus, in [385] it was shown that in the course of regeneration of a platinum catalyst on charcoal in a stream of air at temperatures up to 639°C., the recrystallization of platinum proceeded to a barely perceptible extent:

Time, hr	0	120	240	480	639	—
Crystal size, Å	46	59	52	57	51	54,6

This phenomenon is attributed by the authors of the paper to a complete insulation of the fine platinum crystals from one another by particles of the carrier.

By hindering the process of sintering of fine metal crystals in low-percentage catalysts, the carrier substantially raises their recrystallization temperature as compared with platinum metal. For platinum sponge, the mobility of the atoms already becomes appreciable at 350°C. [356], and at 370-380°C. an exothermic effect is observed which is explained by the recrystallization of fine crystals [357, 358].

It should be noted that platinum undergoes recrystallization more readily in atmospheric air than in nitrogen [355].

If the temperature is raised above 650°C. and the training time is extended, the platinum crystals on aluminum oxide [194, 352, 353] coarsen appreciably as a result of an increase in surface diffusion. This process is also considerably affected by the initial dispersity of the metal in the fresh sample. Other things being equal, subcrystalline samples or contacts with a low content of metals are deactivated less than obviously crystalline ones with a high content of platinum, for example [423, 424, 425] on charcoal or silica gel. V. P. Lebedev et al. [425] note that the most dilute platinum catalyst on silica gel ($\alpha = 0.001$) did not change its activity at all with time during heating. Ref. [269] also indicates that adsorption (0.0054-0.035 wt. %) platinum catalysts did not display any tendency toward a temperature-induced decline of activity; on the contrary, at 700°C., the activity of the most dilute catalyst was three times the original value. These facts were expounded and accounted for by G. I. Yemel'yanova and S. Khasan [386]. They noted that the sintering of adsorption catalysts (dilute metal layers) at high temperatures (700-800°C.) may involve the dissociation of the subcrystalline phase formed earlier and of the coarsened ensembles as a result of a sharp increase in the mobility of the atoms on the carrier and their dispersal over the still-unoccupied surface. Rapid cooling of such a sintered contact leads to freezing of the atoms or their groups on the carrier, with an increase of the metal surface and specific activity. The authors postulate that the discovered phenomenon is characteristic of low-percentage catalysts used at high temperatures. A partial restoration of the initial dispersity of the platinum catalyst on aluminum oxide after its reactivation at high temperature is also reported in [422].

The results obtained are apparently related to the special properties of finely dispersed particles in general and during their stabilization by the carrier in particular. This is supported by the results obtained by N. I. Kobozev, K. Ivanov and P. Bessalov [389, 390] in a study of the oxidation of carbon monoxide on iron and copper aerosols. The authors showed that in contrast to powders, aerosol particles did not coarsen as the temperature was raised, but became finer. Copper oxide aerosol, whose crystals were one order of magnitude smaller than those of copper oxide powder, had a higher activity and adsorptive capacity for oxygen. The specific activity of copper oxide aerosol was 1000 times greater than that of the powder. The process of oxidation of carbon monoxide in the presence of aerosols began 200°C. lower than on the oxide powders.

It is quite probable that the anomaly in the effect of sintering on finely divided metal particles also exists in the case of low-percentage carbon monoxide oxidation catalysts, which operate in a stream of exhaust gas, when the temperature undergoes an abrupt change (200-800°C.) as the operating conditions of the engine vary, resulting in a hardening of the samples.

It appeared of practical interest to elucidate the influence of possible stronger overheatings (up to 900°C.) on the activity, structure and phase composition of a low-percentage palladium catalyst used for removing carbon monoxide and other components from exhaust gases, and on the conditions of its regeneration. A special series of experiments was set up: after a half-hour oxidation of 1% carbon monoxide in a mixture with air at 150, 200, 300, 400, 500, 600, 700, 800 and 900°C., the activity of the catalyst was determined in the same reaction at 200-400°C. (Fig. 32). The experiments showed that at the oxidation temperature of carbon monoxide (300-400°C.), overheatings of the catalyst up to 900°C. practically do not decrease the extent of elimination of CO: the latter is 90-100% oxidized. The activity of the catalyst at a lower temperature (200-250°C.) decreases by 20-23% after being used at 700-900°C.

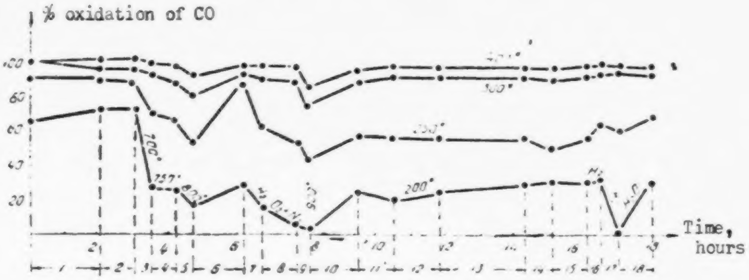


Fig. 32. Effect of overheatings (half-hour each) to 900°C. and of gas treatment on the activity of palladium catalyst on aluminosilicate in the oxidation reaction of 1% CO in air at 200-400°C. [61]. 1 - 150, 200, 300, 400°C. in a stream of 1% CO, 0.5 hr; 2 - 500, 600°C. in a stream of 1% CO, 0.5 hr; 3 - 700°C. in a stream of 1% CO, 0.5 hr; 4 - 750°C. in a stream of 1% CO, 40 min; 5 - 800°C. in a stream of 1% CO, 0.5 hr; 6 - 3% CO + 10% O_2 + N_2, 400°C., 1.5 hr; 7 - H_2 at 250°C; 8 - air, 400°C.; 9 - 900°C., 1% CO, 20 min; 10 - 3% CO + 10% O_2 + N_2, 400°C., 1.5 hr; 11 - 3% CO + 50% O_2 + N_2, 600°C., 1 hr; 12 - 5% O_2 + N_2, 400°C.; 13 - 3% CO + 10% O_2 + N_2, 400°C.; 14 - 3% CO + 10% O_2 + N_2, 600°C.; 15 - 6% CO + 10% O_2 + N_2, 400°C.; 16 - H_2, 300°C.; 17 - H_2, 350°C.; 18 - H_2O_2.

The decrease in the activity of the palladium catalyst after overheatings in a stream of air at 700-800°C. may be explained by a number of factors, the chief ones being a decrease in the total and specific surface of the catalyst and the oxidation of palladium to the oxide. It is known that the temperature of the start of an intensive migration of fine metal crystals over the surface with formation of coarser crystals on such carriers as asbestos, zinc oxide and others amounts to approximately 0.4-0.5 of the melting point of the metal [354, 391]. In the case of palladium, it is close to 770°C. On the other hand, at 800-900°C., a change is possible in the porous structure of aluminosilicate, whose maximum calcination temperature during preparation is 800°C.

It is known from the literature [349] that when palladium is treated with oxygen for an extended period (20 hours), metallic films of palladium can be oxidized at a temperature as low as 250°C. At the same time, about 30 monolayers of oxygen are absorbed. The possibility of the appearance of a phase oxide is also indicated by the closeness of the values of the heats of chemisorption of oxygen on palladium black (-24.0 kcal/mole of oxide in the 500-700°C. range for a degree of surface coverage of 1×10^{-4} to 0.7) and formation of surface (-24.6 kcal/mole of oxide) and volume (-21 kcal/mole) palladium oxides [350]. To elucidate the causes of the partial deactivation of palladium catalyst, its phase composition, change of structure, and surface area were studied in the course of the above-indicated treatment and regeneration of the contact.

Phase x-ray structural analysis was carried out on six samples of palladium catalyst on aluminosilicate (0.75% Pd): 1) after use at 700°C. in a stream of 1% CO in air; 2) after treatment at 900°C. with a mixture of 5-6% CO + 3% O_2 + N_2; 3) after treatment with H_2O_2; 4) original sample activated in a stream of air for 0.5 hr at 400°C.; 5) after testing for stability to overheatings (600-900°C.); 6) after use for 2 hours on stand of MZMA-407 engine.

Results of the phase x-ray structural analysis are given in Table 21. The x-ray data showed that palladium was present in the crystalline state in all the samples.

It is evident from the tabulated data that after their use at 700°C. in a stream of 1% carbon monoxide, the palladium catalyst samples on bead aluminosilicate contained chiefly palladium oxide. The results of x-ray diffraction patterns for samples Nos. 2 and 4, not illustrated here, also show the presence of a large amount of palladium oxide along with palladium.

Data for sample No. 5, tested for a long period of time in a laboratory unit during oxidation of carbon monoxide in a stream of air are particularly illustrative. In this case, no lines characteristic of palladium metal were observed, and a new phase, palladium oxide, was formed. Similar data were obtained by analyzing a sample of catalyst No. 6, used on the gasoline engine stand.

Suggestions concerning the possibility of formation of platinum and palladium oxides in oxidative catalysis (decomposition of hydrogen peroxide, oxidation of sulfur dioxide, and other processes) can be found in the literature [359-362]. However, no concrete data are given for supported catalysts. The data obtained indicate that palladium oxide, like palladium, is able to activate carbon monoxide and oxygen on its surface, i.e., function (as do oxides of nonprecious metals) as a carbon monoxide oxidation catalyst. This is confirmed in [162] by the example of activated adsorption of carbon monoxide on palladium oxide, which ends in the desorption of carbon dioxide.

Table 21

Phase Composition of Catalysts

Intensity I	d/n— Interplanar Spacing			Phase
	Found	Tabular Data		
		For Pd [351]	For Glass	
Sample 1. Fe, K_α, 30/15, 15 hours				
6	2,65	2,644 (10)	—	Palladium oxide
1	2,17	2,153 (2)	—	»
3	1,67	1,674 (3)	—	»
2	1,54	1,536 (2)	—	»
3	1,31	1,322 (2)	—	»
1	1,08	1,080 (1)	—	»
Sample 3. Cu, K_α, 30/15, Ni filter, 8 hours				
3	2,665	2,644 (10)	—	Palladium oxide
10	2,642	2,644 (10)	—	»
10	2,256	—	—	Palladium
2	2,157	2,153 (2)	—	Palladium oxide
5—6	1,954	—	—	Palladium
3—4	1,683	1,674 (3)	—	Palladium oxide
1—2	1,538	1,536 (2)	—	»
1—2	1,522	1,536 (2)	—	»
3—4	1,378	—	—	Palladium
3—4—2	1,326	—	—	»
3—4	1,174	—	—	»
1	1,127	—	—	»
Sample 5. Cu, K_α, 30/15, Ni- filter 7,5 hours (recorded on glass mount)				
Amorphous halo				
3	3,140	—	3,156 (3)	Glass
10 m	2,697	2,644 (10)	—	Palladium oxide
2	2,443	—	2,499 (2)	Glass
2	2,177	2,153 (2)	—	Palladium oxide
3—4	1,841	—	1,844 (3)	Glass
6	1,691	1,674 (3)	—	Palladium oxide
7—8 m	1,542	1,536 (2)	1,524 (4)	»
7—8 m	1,325	1,322 (2)	—	»
1	1,137	1,135 (1)	—	»
1	1,085	1,0806 (1)	—	»
1	1,006	1,007 (2)	—	Palladium oxide
1	0,966	0,962 (1)	—	»
1	0,905	0,905 (1)	—	»
Sample 6. U — 35 κV, $I = 20$ mA, $i = 12$ $D = 57{,}3$ mm $d = 0{,}7$ mm				
10	2,673	2,667 (33)	—	Palladium oxide
1	2,157	1,153 (20)	—	»
4	1.683	1,674 (28)	—	»
3	1,538	1,536 (18)	—	»
3	1,322	1,322 (12)	—	»
2	1,080	1,081 (9)	—	»
2	0,993	0,998 (6)	—	»
1	0,905	0,9053 (6)	—	»
1	0,834	0,840 (6)	—	»

In the case of low-percentage platinum catalysts, x-ray phase analysis failed to detect any platinum oxide. Apparently, even if a partial oxidation of platinum does occur during the action of oxygen on the supported platinum catalyst [322], it does so without forming phase oxides. This differentiates the low percentage catalyst from platinum black, the activation of the surface of which at 400-600°C. is attributed to the formation of phase oxides [268]. Oxide films were formed during heating of a platinum plate to 800°C. and above in the presence of oxygen [365] and also during the oxidation of ammonia in the presence of water vapor at 750°C. [366] and sulfur dioxide [361, 367]. The appearance of Pt_3O_4 as a result of treatment with an explosive gas mixture at 600°C. did not cause any marked changes in the catalyst's activity [365]. Under the influence of oxygen, the compact film undergoes an exothermic phase transformation at 500-600°C. [268]. These data attest to the possibility of a phase formation of platinum oxides when a compact metal is used.

Admixtures of platinum in supported palladium impart to the latter a stability to oxidation. Palladium oxide was not detected in a sample of mixed platinum-palladium catalyst (0.5% Σ Me) used for 4-6 hours in a stream of exhaust gas from "Moskvich-407".

In order to obtain a partial reduction of palladium oxide, the catalyst was treated with a mixture of 3% carbon monoxide and 10% oxygen in nitrogen at 400°C. for 1.5 hours. Favorable conditions were thus created for the regeneration of palladium. As is evident from Fig. 32, it was possible to raise the degree of oxidation of carbon monoxide at 200°C. to 30%, and at 250°C. to 85-90%.

The positive influence of the reacting mixture was observed in the regeneration of a catalyst which was used at 900°C. (Fig. 32, see sections 10 and 18).

The x-ray pattern of a catalyst treated with hydrogen peroxide (sample 3) also shows the reduction of a part of the palladium oxide to the metal. Unfortunately, treatment with hydrogen of a catalyst which has partially lost its activity failed to yield positive results (Fig. 32, see section 7, 16 and 17). This is apparently due to a strong adsorption of hydrogen on the catalyst surface, preventing the chemisorption of carbon monoxide. A brief (25 min) oxidation of carbon monoxide in high concentrations (5-6%) at a relatively low oxygen content (3%) in a nitrogen mixture which approximated the composition of the exhaust gas of gasoline engines did not deactivate the catalyst even at 900°C. (Fig. 33).

X-ray patterns of a catalyst used in mixtures with a relatively high content of carbon monoxide indicate the reduction of a part of palladium oxide to the metal during regeneration.

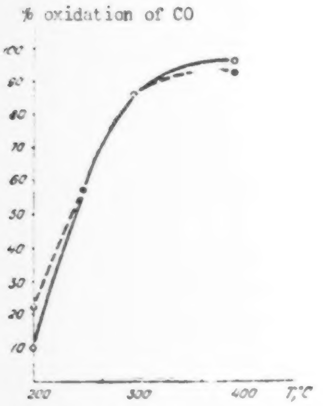


Fig. 33. Influence of brief (25 min) treatment of palladium catalyst on synthetic aluminosilicate in a mixture of 6% CO + 3% O_2 + nitrogen at 900°C. on its activity at lower temperatures. Solid line - after overheating; dashed line - before overheating.

Thus, despite a partial decrease in the activity of the palladium catalyst on aluminosilicate at low temperatures (200-250°C.) after the catalyst has been used at 700-900°C., and because of its oxidation with the formation of palladium oxide, which continues to catalyze the process, the degree of oxidation of carbon monoxide may increase when the catalyst is treated with hydrogen peroxide or a mixture of 3-6% carbon monoxide, 5-10% oxygen and nitrogen, i.e., a mixture whose composition is close to that of the exhaust gas under certain operating conditions of the engine.

The above data permit one to postulate that the state of palladium in the catalyst and its activity under the conditions of operation prevailing in a gas purifier in a stream of exhaust gas with a high concentration of carbon monoxide and hydrogen will depend on the composition of the gas mixture. At a relatively high oxygen concentration (up to 20%) and high temperatures, palladium oxide will be active, at a high content of carbon monoxide and hydrogen and a lower oxygen concentration (5-10%), palladium metal will be active, and thus during overheatings the contact will be sufficiently stable, since it will be steadily regenerated. In the processes of road testing of palladium catalysts, these assumptions were subsequently confirmed experimentally.

In addition to studying the chemical state of palladium during prolonged service with a steadily rising temperature, we investigated the change of the total surface and structure of the catalyst. It is known that as the catalyst is used, its structure undergoes changes caused by the action of high temperatures, water vapor, coke (cracking contacts) [369], soot (catalysts for neutralizing exhaust gases) and other factors. γ-Aluminum oxide is characterized by gradual sintering of the surface as the calcination temperature is raised, such that at 900-1000°C. there is a sharp decrease in surface and a substantial alteration of the porous structure, which converts to corundum [370]. The greatest structural changes occur in fine-pored samples with an extended surface. The fine-pored structure of silica gel is also unstable [317]. The introduction of aluminum oxide into the silica gel lattice markedly alters the surface properties of the aluminosilicates formed as compared with the original oxides [372]. Steam treatment of cracking catalysts at 750°C. decreases their total surface as a result of a reduction in the number of pores due to the destruction of the walls by the fusion and coarsening of the pores [373]. In the absence of water vapor at high temperature, the surface of the aluminosilicate catalyst is decreased by uniform sintering of all the pores, and the distribution maximum of the pore volume shifts slightly toward larger radii. Some authors have noted a rapid sintering of the bead aluminosilicate catalyst starting at 900°C. [374, 375].

In order to elucidate the influence of heat treatment of the palladium catalyst on aluminosilicate on the surface area and structure of its pores, isotherms of adsorption and desorption of benzene at 20°C. were plotted by the Rubinshteyn-Afanas'yev method [376-378]. The surface area was calculated from the adsorption branch of the curves using the BET equation, and the distribution of the pore volumes over the radii was calculated from the inverse branch of the isotherm without considering the thickness of the adsorption film of the adsorbate.

Data from the study of the porous structure of the catalysts are presented in Figs. 34 and 35 and in Table 22.

Table 22 lists data on the surface area of the initial catalysts, determined from the BET equation with four points for low-temperature adsorption of air [379] and with two points for low-temperature adsorption of argon, and also by chromatography [380]. Comparison of the surface areas shows that they are similar and agree with the reported data on the surface area of bead aluminosilicate, 330-360 m^2/g [380, 373]. Hence, the surface area of the carrier for a small degree of coverage by the metal underwent practically no changes.

An examination of the general form of the benzene adsorption isotherms suggests that both the initial palladium catalyst on bead aluminosilicate and the initial carrier [373] have a transition-porous structure (Figs. 34, 35). The width of the hysteresis loop for catalysts used at 700 and 900°C. is considerably narrower than for the catalyst in the presence of which the oxidation of carbon monoxide was carried out at 400°C. This fact attests to a certain dilation of the catalyst pores after the reaction was carried out at 700 and 900°C.

The total volume of the pores (see Table 22) in these catalysts ranges from 0.61 to 0.52 ml of benzene/1 g of catalyst, but on the other hand there is a sharp decrease in the volume of the finest pores (less than 20Å), i.e., from 0.25 to 0.09 at 700°C. and to 0.02 at 900°C.

Comparison of the curves of pore distribution over radii (Fig. 35) for catalysts tested under different conditions shows that the structure of the catalysts changes substantially at high temperatures. Whereas in the sample after tests at 400°C. the bulk of the pore volume is accounted for by pores with r = 20-30 Å, the number of pores in the catalyst in the presence of which

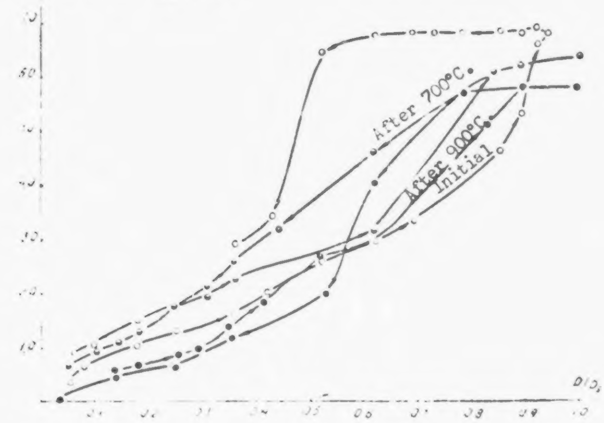


Fig. 34. Isotherms of adsorption and desorption of benzene vapor at 20°C. for a palladium catalyst on synthetic aluminosilicate (0.5 wt. % Pd).

Table 22

Surface and Distribution of Pore Volumes Over Radii for Palladium Catalyst on Synthetic Aluminosilicate (0.75 wt. % Pd) in the Course of Use.

Conditions of Treatment of Catalyst	Surface, m^2/g			Pore Volume, cm^3 of Catalyst				Total Pore Volume
	For Benzene	For Air	For Air Chromatographically	0—20 Å	20—30 Å	30—50 Å	Above 50 Å	
After oxidation of CO at 400°C.	366	335	386	0,2539	0,3175	0,0224	0,0188	0,6100
After oxidation of CO at 700°C.	425	412	—	0,1923	0,0047	0,1925	0,1806	0,5690
After oxidation of CO at 900°C.	260	260	372	0,1039	0,0223	0,2533	0,1415	0,5210
Activated* in a stream of air at 400°C.	—	366	380	Unknown	—	0,3800	0,4400	0,8550
After use* in ZIL-130 automobile, 21,000 km	—	271	341	*	—	0,2400	0,6760	0,9000
Initial carrier	—	334 359 378	322					

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* The distribution of pore volumes over radii was obtained on a porometer.

the oxidation took place at 700°C. was greatly reduced (by a factor of 60). Moreover, there appear a considerable number of pores with radii of 30-50 Å or more. After the oxidation of carbon monoxide at 900°C., the volume of pores with radii up to 20-30 Å also decreases as compared to the initial sample, and the number of larger pores increases (Table 22).

This is also indicated by comparative data on the distribution of the pore volumes over radii (obtained with a pore-measuring device) for the initial palladium catalyst and a catalyst used in a stream of exhaust gas in a gas purifier mounted on a ZIL-130 automobile which traveled about 21,000 km (Table 22 and Fig. 36).

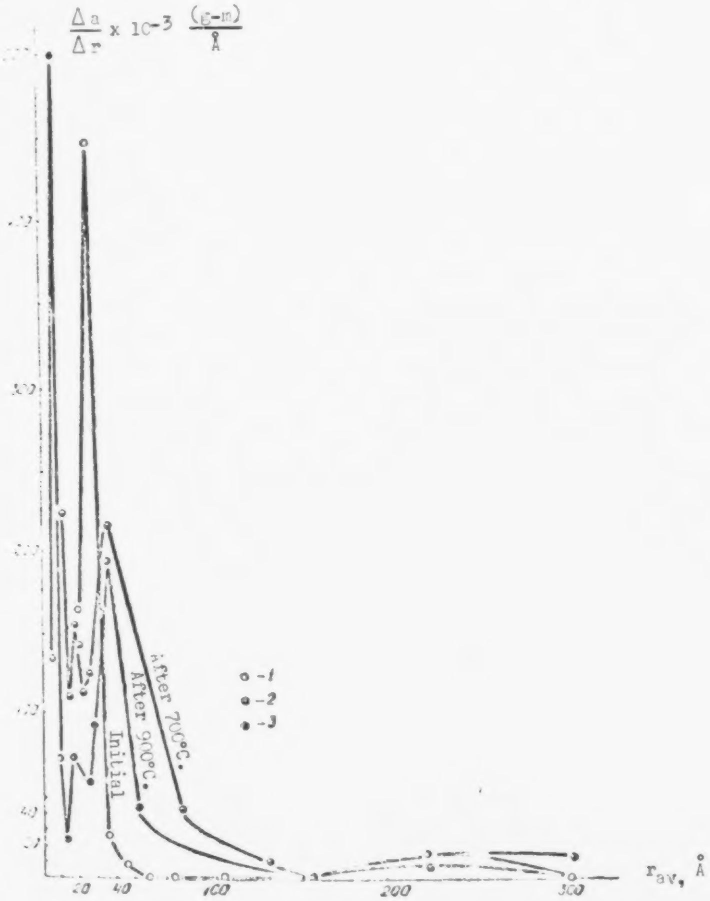

Fig. 35. Curves of distribution of pore volumes over radii for samples of palladium catalyst on synthetic aluminosilicate after tests at: 1 - 400°C.; 2 - 700°C.; 3 - 900°C.

Thus, raising the oxidation temperature of carbon monoxide to 700-900°C., both in laboratory experiments and in a stream of exhaust gas, causes a rearrangement of the structure of the palladium catalyst on aluminosilicate and a slight change of the total pore volume.

Calculation of the area of the catalyst samples studied showed that as the oxidation temperature of carbon monoxide is raised to 700-900°C. and in operational tests of the palladium catalyst on aluminosilicate, a decrease in its area of approximately 30% takes place.

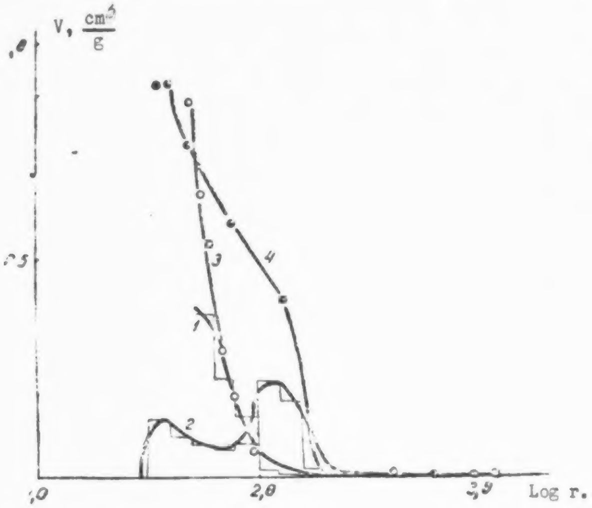

Fig. 36. Differential (1, 2) and integral (3, 4) curves of distribution of pore volumes over equivalent radii of palladium catalyst on synthetic aluminosilicate (0.75 wt. % Pd), obtained by mercury porometry. 1, 3 - sample after activation in a stream of air at 400°C.; 2, 4 - after tests in a stream of exhaust gas of ZIL-130 engine in the course of 21,000 km.

Summing up the results of studies of the atability, phase composition, and structure of low-percentage platinum, palladium, and platinum-palladium catalysts for oxidizing carbon monoxide, we can state the following. At temperatures up to 700°C., the contacts operate stably for a long period of time, this being due to their high stability to recrystallization. Starting at 700-900°C., heating in air causes a reduction of the total area of the catalyst as a result of sintering of fine pores, a partial oxidation of palladium to the oxide, and a 20-40% decrease in the degree of oxidation of carbon monoxide at a reaction temperature of 200-250°C. The activity of the contact at a higher temperature is close to 100%. It is possible that during the sintering of the pores, the palladium concentration on the carrier decreases slightly, and because of this phenomenon, the activity of the catalyst cannot be fully restored to its original value at a low temperature.

It is also possible, as suggested by some authors [381], that a slight deactivation of the catalyst is caused by a coarsening of the palladium oxide crystals which is accelerated in the presence of oxygen.

Chapter 4

COMPLETE CATALYTIC OXIDATION OF HYDROCARBONS

The catalytic oxidation of hydrocarbons is carried out for the purpose of obtaining intermediate organic compounds that are of considerable importance in industrial organic synthesis. The oxidation of hydrocarbons to carbon dioxide and water is a side reaction, and had received little attention in the literature until the 1950's. Studies in the field of complete catalytic oxidation of hydrocarbons are now being expanded in view of the utilization of this reaction in fuel cells operating on natural gas and in the removal of hydrocarbons from the exhaust gases of internal combustion engines and chemical plants. The catalytic method of complete oxidation of hydrocarbons is also used in the generation of heat used for heating certain installations and for motor transport in the Far North. The use of catalysts for the combustion of organic discharges permits a substantial lowering of the oxidation temperature and of the cost of building and heating the installations that burn noxious substances at various chemical plants.

Results of known research in the field of complete catalytic oxidation of hydrocarbons are presented in Table 23.

Analysis of the studies shows that the substances subjected to oxidation were chiefly saturated and unsaturated open-chain hydrocarbons (acetylene, ethylene, methane, and their derivatives), cyclic (cyclohexane) and aromatic (benzene) compounds, and also compounds containing atoms of nitrogen, oxygen, and halogens in their composition. The hydrocarbon concentrations were determined by the specific conditions of the various processes, for example, in the case of acetylene, up to 0.005%; hydrocarbons of cracking gases, up to 0.07-0.08%; and automobile exhaust gases, from 0.15 to 1.0%. The activity and type of the catalysts employed depend primarily on the temperature and nature of the organic compounds.

The problem of influence of the structure of organic compounds on the temperature of their catalytic oxidation to CO_2 and H_2O has been treated in a number of interesting studies [96, 98, 111, 112, 143]. Accomazzo and Nobe [111] showed that the oxidation rate of hydrocarbons in a stream of air to CO_2 and H_2O over CuO/Al_2O_3 catalyst at a space velocity of 525 l/hr slows down with decreasing number of carbon atoms in the molecule (ethane, propane) and accelerates with increasing degree of unsaturation of the molecule (ethane, ethylene, propane, propylene, propadiene) and decreasing number of carbon atoms in equally unsaturated compounds (acetylene, propyne).

The oxidation of such hydrocarbons as acetylene, propyne, propadiene, propylene, ethylene, propane, cyclopropane, and ethane is 80% complete at the following temperatures: 200, 230, 240, 228, 310, 380, 400 and 420°C.

Table 23.

Complete Catalytic Oxidation of Hydrocarbons.

Composition of catalyst	Composition of gas mixture	Space velocity, hr^{-1}	% oxidation								Characteristics of catalysts and process	Reference
			150°	200°	300°	350°	400°	500°	550°	600°		
1	2	3	4	5	6	7	8	9	10	11	12	13
Hopcalite	20-125 mg/1 of hydrocarbons in air	—	—	—	—	—	—	—	—	—	Halogen- and nitrogen-containing compounds are not oxidized completely	[96]
	Benzene	21	—	74	87	92	—	—	—	—		»
	1, 2, 4-trimethylbenze	»	—	55	98	100	—	—	—	—		»
	Butylbenzene	»	—	86	[illegible]	96	—	—	—	—		»
	n-Hexane	»	—	77	97	97	—	—	—	—		»
	n-Decane	»	—	89	98	96	—	—	—	—		»
	2,2-CH$_3$-butane	»	—	40	84	98	—	—	—	—		»
	1-Octene	»	—	83	89	94	35—40	—	—	—		»
	Methanol	»	—	95	98	98	—	—	—	—		»
	Methane	»	—	—	—	—	—	—	—	—		»
	Cyclohexane	»	—	—	—	91	—	—	—	—		»
	Methane	»	—	—	—	—	50	—	—	—		»
	Hexane	»	—	—	97	—	—	—	—	—		»
	Dioctyl phthalate	»	—	—	97	—	—	—	—	—		»
		»	—	—	100	—	—	—	—	—		»
	Triaryl phosphite	»	—	—	100	—	—	—	—	—		»

Continuation of Table 23

Cr_2O_3/pumice	Hydrocarbons in air											
	Ethane, ethylene	—	—	—	—	—	—	—	100	—		[95]
	Propane, benzene	—	—	—	—	—	—	100	100	—		»
	Butane, toluene, pentane, hexane, octane	—	—	—	—	—	—	—	—	—		»
	Methane	—	—	—	—	—	—	—	100	100		»
CuO/Al_2O_3 (1:1)	~0,15 % in air	160—525 l/hr, 25 ml of catalyst	—	—	—	—	—	—	—	—	Catalyst resistant to moisture, used for 1000 hr	[111]
	Acetylene		—	80	—	—	—	—	—	—	—	»
	Propyne		—	80	—	—	—	—	—	—	—	»
	Propadiene		—	80	—	—	—	—	—	—	—	»
	Propylene		—	—	80	—	—	—	—	—	—	»
	Ethylene		—	—	80	—	—	—	—	—	—	»
	Propane		—	—	—	—	—	—	—	—	—	»
	Cyclopropane		—	—	—	—	80	—	—	—	—	»
	Ethane		—	—	—	—	80	—	—	—	—	»
	Methane		—	—	—	—	80	—	80	—	—	»
Cu/Al_2O_3 (1:1)	190–2000 parts per million of cyclohexane in air	31580	—	—	20	55—60	—	—	—	—	Rate constant of complete oxidation decreases from benzene to cyclohexane and cyclohexene	
Co_3O_4	5.7×10^{-5} mole, various hydrocarbons	50 ml of catalyst, space velocity unknown	100	100	—	—	—	—	—	—		[145] [112]

Continuation of Table 23

1	2	3	4	5	6	7	8	9	10	11	12	13
V_2O_3	2-CH_3-butane											
	Benzene	»	—	—	—	—	—	—	—	100	—	»
	n-Pentane		—	—	—	—	—	—	100	100	—	»
	n-Hexane	»	—	—	—	—	100	—	—	—	—	»
	1-Pentyne	»	—	—	—	—	100	—	—	—	—	»
Co_3O_4	2-CH_3-butane	»	—	100								
MnO_2	»	»	—	—	100	—	—	—	—	—	—	»
Cr_2O_3	»	»	—	—	—	100	—	—	—	—	—	»
NiO	»	»	—	—	—	100	—	—	—	—	—	»
Fe_2O_3	»	»	—	—	—	100	—	—	—	—	—	»
CeO_2	»	»	—	—	—	—	—	100	—	—	—	»
W_2O_5	»	»	—	—	—		—	100	—	—	—	»
Al_2O_3	»	»	—	—	—	—	100	—	—	—	—	»
ThO_2	»	»	—	—	—	—	100	—	—	—	—	»
CuO	»	»	—	—	—	—	—	100	—	—	—	»
V_2O_5	»	»	—	—	—	—	—	—	—	100	—	»
Fe_2O_3—CuO Clay	0.45% of propane-butane mixture in air	36000	—	—	12	—	65	80	—	—	—	[58]
CuO—Cr_2O_3 Clay		»	—	—	12	35	52	75	—	—		[58]
Active MnO_2	2 x 10^{-4}% of acetylene in oxygen-argon fraction of compressed air	60000	100	—	—	—	—	—	—	—	Deactivated by water vapor	[92]
Commerical MnO_2	0.002-0.2% of acetylene in oxygen	5000—20000	80—96	97—99	100	100	100	—	—	—	—	[99]

Continuation of Table 23

Pyrolusite Mn ore promoted with 1% Ag_2O and $AgMnO_4$	0.005 % in air	60000	83— —100	—	—	—	—	—	—	—	Stable to water vapor, carbon dioxide, sulfur oxides, nitrogen oxides, ammonia; poisoned with traces of compressor oils	[92— —94]
CoO_2	Ethylene	Contact time 0.3 sec, volume of catalyst 0.5 ml. Space velocity ≈ 500	—	—	—	—	100	—	—	—	—	[109]
Oxides of cobalt + silver	Ethane, ethylene, propane propylene, acetylene, butylene in air	1-30 at P = 300 atm	100	—	—	—	—	—	—	—	—	[107]
Oxides of cobalt + silver		Up to 20,000 at P = 50-300 atm	100	—	—	—	—	—	—	—	—	[108]
Oxides of Mn and Fe on grog	3.18% methane, 1.5% H_2, 16.5% O_2	450	—	—	—	—	—	60	—	95		[141]
Barium chromite on carriers (Al_2O_3, SiO_2)	Isobutane, n-butane	2200—7200	—	—	—	—	—	—	—	—	—	[133]
Pd on synthetic aluminosilicate	0.5% of cyclohexane in air	6000—12000	—	10	85—95	—	—	—	—	—		Data of GIAP, IKhN AN KAZ SSR

Continuation of Table 23

1	2	3	4	5	6	7	8	9	10	11	12	13
•	0.5% cyclohexane, 1% carbon monoxide in air	6000—8000	30	65	90	—	—	—	—	—	—	
$\frac{Pt+Pd}{Al_2O_3}$ $\Sigma Me=1$ %	Up to 3% methane in air	—	—	—	—	—	—	—	—	—	Start of oxidation at 300°C., used for analytical purposes	[103]
Pt/ aluminosilicate	1% propane-butane fraction of cooking gas (78% propane, 13.3% butane, 5.5% ethane, 4% methane) in air	36000	—	5	30	—	80	96	100	—		[57]
Platinum on Al_2O_3 (AP-56)	Waste gas of synthetic acid plant	Up to 3000 1/kg hr	—	—	At 300-350°C. odor disappears						—	[105]
Platinum on refractory alloy strip	CO, H_2 and organic compounds	—	—	—	—	—	—	—	—	—	CO, H_2 and organic impurities completely oxidized. Catalyst destroyed in the presence of large amounts of inorganic solids in the gas	[101]

Continuation of Table 23

Platinum on ceramic rods (Houdry "oxicat")	Waste gases of roasting furnaces, regeneration gases of petroleum refineries, etc. C_3H_{10}-0.07 -0.08 %, O_2-19.5 %, H_2O-2.5-2.7 %, CO-2.5 %	—	—		Complete oxidation						Service life of gas purifier, 2500 hr. Units operate for 6000 hr using the heat of exhaust gases	[104]
Platinum on screens, stainless steel perforated plates, or on Al_2O_3	Waste gases of chemical plants	—	—		Complete oxidation						Units utilizing the heat evolved by the oxidation are advantageous	[102]
Platinum, palladium, rhodium, ruthenium on carrier	1.5% methane, 3% oxygen, 95.5% nitrogen	100000— —200000	—	—	Complete oxidation achieved at 400-500°C.							[106]

Continuation of Table 23

1	2	3	4	5	6	7	8	9	10	11	12	13
Activated alumina (85% Al_2O_3)	0.02–0.25% hydrocarbons (61.7% CH_4, 14.7% ethane, 23.5% heavy hydrocarbons in the krypton-xenon fraction)	400	—	—	—	60–80% purification achieved at 500–600°C.					Catalyst served for several years under industrial conditions	[394]
CuO/Al_2O_3 (1:1)	1-Hexene (1170 ppm	$4 \cdot 10^3$	—	—	—	—	100	—	—	—	Catalyst tested for oxidation of CO and hydrocarbons in exhaust gases for 100 hrs.	[89]
		$10 \cdot 10^3$	—	—	—	—	90	—	—	—		
		$16 \cdot 10^3$	—	—	—	—	80	—	—	—		
		$16 \cdot 10^3$	—	35	—	—	—	—	—	—		

The reaction rate increases with rising temperature and concentration of the hydrocarbons and decreasing space velocity. A similar relationship between the structure and rate is observed in noncatalytic oxidation of hydrocarbons [203].

In experiments involving the complete oxidation of hydrocarbons on hopcalite, Johnson and Christian [96] showed that a total increase of the molecular weight of hydrocarbons facilitates the reaction. Methane is the most difficult to oxidize: at 450-500°C., the oxidation is only 35-50% complete. Bransom and Haulon [143] observed a similar relationship in a study of the influence of the structure of paraffin hydrocarbons on the kinetics and mechanism of their complete oxidation on copper oxide (Fig. 37). From the results obtained by the authors it is evident that as the chain length increases, the oxidation of the hydrocarbons becomes easier. Among hydrocarbons included in the composition of automobile exhausts, the most difficult to oxidize are unsubstituted saturated hydrocarbons, particularly those of isomeric structure (pentane, hexane, 2-methylbutane) and also benzene [112].

In a study of the oxidation of hydrocarbons on oxide catalysts, Stein et al. [112] showed that the reactivity of hydrocarbons with the same number of carbon atoms increases in the following sequence: aromatic hydrocarbons, isoparaffins, straight-chain paraffins, olefins, and acetylenic compounds.

Similar data were obtained by V. N. Vendt and T. A. Lebedeva [95], who used chromium oxide deposited on pumice for the analysis of a series of organic compounds. A complete oxidation of methane on this catalyst is achieved at 650-700°C., ethane and ethylene at 550°C., propane and benzene at 500°C., butane and toluene at 450°C., and pentane, hexane, octane, and amylene at 400°C.

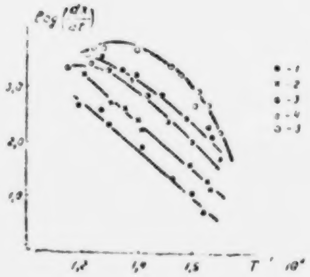

Fig. 37. Oxidation of paraffin hydrocarbons on cupric oxide: 1 - methane; 2 - ethane; 3 - propane; 4 - pentane; 5 - C_{6-7} - paraffins (hexane, 2,2-dimethyl-butane, heptane, 2,3-dimethylpentane)[143].

Economy and Mellon [133] indicate the high activity of barium chromate on carriers at space velocities of 2.2-7.2 x 10^3 hr^{-1}. A complete oxidation of n-butane, isobutane and isobutene on this contact takes place at 350-450°C. Isobutene oxidizes at the fastest rate, followed by isobutane and n-butane. Barium chromate is stable to overheating at 600-800°C. and operates for a long time without a decrease in activity (600°C. - 168 hours, 700°C. - 48 hours, 800°C. - 24 hours).

The oxidation temperatures of oxygen-containing compounds (alcohols, ketones, aldehydes) are similar. Thus, T. G. Alanova and L. Ye. Margolis showed [171] that for the same contact time of 0.34-0.37 sec, the oxidation temperature of several compounds differs by 50°C.: acetone, phenol, methanol (473°C.), butyraldehyde (443°C.), diacetone alcohol (523°C.).

In addition to their structure, the chemical composition of catalysts has a considerable effect on the temperature of complete oxidation of hydrocarbons. Most illustrative in this respect are the results obtained by Stein et al. on metal oxides [112]. By oxidizing seven hydrocarbons on twelve oxides of polyvalent metals, they obtained a general relationship whereby the temperature of complete oxidation increased in a given sequence of oxides for the majority of the hydrocarbons studied. Figure 38 shows data on the temperature of complete oxidation of 2-CH_3-butane and n-pentane on catalysts consisting of oxides of different metals. In the oxidation of cyclohexane, the reaction proceeded in the following sequence of metal oxides: vanadium (550°C.), tungsten (540°C.), thorium (350°C.), copper (350°C.), cerium (330°C.), aluminum (300°C.), iron (300°C.), chromium (270°C.), manganese (230°C.), cobalt (150°C.) and in the case of 1-pentyne: vanadium (350°C.), thorium (250°C.), copper (270°C.), cerium (260°C.), chromium (250°C.), tungsten, aluminum (220°C.), manganese (220°C.), cobalt (210°C.), titanium (210°C.), nickel (200°C.), iron (180°C.).

All the hydrocarbons display a common trend, i. e., higher oxidation temperatures as less refractory oxides (those of manganese, iron, cobalt, nickel) are replaced by more refractory ones (those of vanadium, thorium, tungsten), which are characterized by a low partial pressure of oxygne above the oxides.

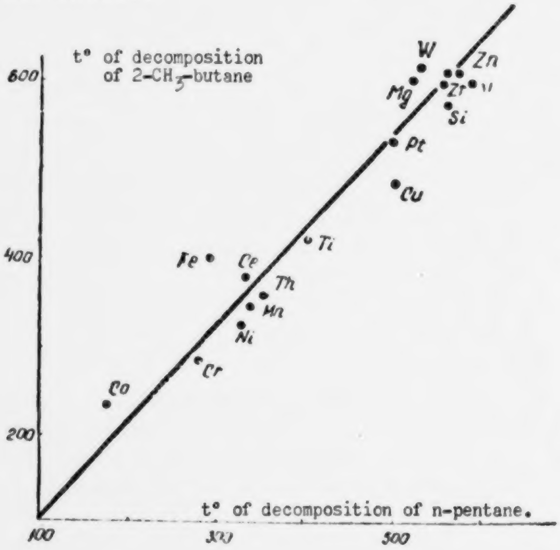

Fig. 38. Oxidation of 2-methylbutane and n-pentane on oxide catalysts [112].

Very similar results on the influence of chemical composition of the oxides were obtained in studies of complete oxidation of ethylene [154, 155]. Dmukhovskiy noted that the oxides Co_3O_4 and Co_2O_3 display the maximum activity, and the reaction rate at 262°C. decreases when oxides of the following metals are used: cobalt, chromium, silver, manganese, copper, nickel, cadmium, iron, molybdenum, vanadium, titanium. When the oxides are deposited on a carrier, their activity increases.

M. Ya. Rubanik et al. [155] found that the oxidation reaction of ethylene in a flow-through circulating unit slows down in the following order of metal oxides: manganese, copper, cobalt, iron, uranium, cadmium, vanadium, nickel, zirconium, lead, tungsten. A slight difference in the sequence of the oxides according to decreasing activity in the works of different authors is apparently due to differences in the conditions of preparation of the catalysts and their use.

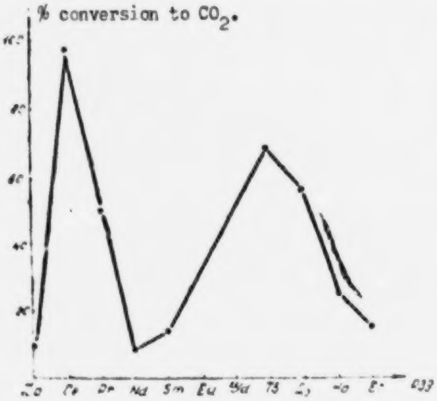

Fig. 39. Percent conversion of propylene to CO_2 at 360°C. as a function of the atomic number of the rare earth element [471].

Kh. M. Minachev et al. [471] showed that on rare earth oxides including oxides of cerium, praseodymium, neodymium and terbium, propylene is completely oxidized. The catalytic activity of rare earth oxides in this reaction is determined by the binding energy between oxygen and the surface of the oxides acting as catalysts. Experiments show that as the atomic number of the elements whose oxides were studied as catalysts changes, the yield of carbon dioxide, i. e., the extent of oxidation of propylene to carbon dioxide and water (at t = 360°C.) changes periodically, passing through two maxima (Fig. 39) characteristic of cerium and terbium oxides. The oxides of neodymium, samarium, dysprosium, gadolinium and turbium have a stable activity in the oxidation reaction of propylene, i. e., the carbon dioxide yield in their presence is virtually constant. Oxides of lanthanum, cerium and praseodymium display a constant activity in the course of the first 30-40 min, and then, depending on the temperature of the experiment, their activity increases sharply. In all cases, a complete oxidation of propylene takes place.

The activity of rare earth oxides is displayed in the temperature range in which the oxygen adsorbed on the surface of these oxides is the most mobile. Active rare earth oxides are associated with the mobility of the oxygen of such oxides as cobaltous-cobaltic oxide, manganese oxide, and nickel oxide, used as oxidation catalysts [408].

The combined effect of the mobility of oxygen and catalytic activity of rare earth elements in oxidation reactions suggests that rare earth oxides can be good oxidation catalysts for other hydrocarbons as well.

S. Z. Roginskiy, L. Ya. Margolis [97, 150, 170], and other authors have advanced certain principles of selection of oxide catalysts for the reaction of complete oxidation of hydrocarbons. They showed that in the oxidation of isooctane, cyclohexane, and other compounds, the oxides of transition elements and faintly colored oxides of such transition elements as niobium, molybdenum, etc., have a weak activity. The activity of individual oxides of transition elements decreases rapidly in the course of service, whereas binary oxides containing at least one transition element and forming colored compounds are marked by a high activity.

The authors note further that the most active and stable systems (particularly when deposited on a carrier) are spinels, whose properties were studied in detail. The more pronounced oxidizing properties of chromium spinels (as compared to others) are mentioned (Table 24).

On copper chromium and magnesium-chromium catalysts, isooctane burns up most readily, followed by cyclohexane and methylcyclohexane [146].

The high activity of copper chromite in the oxidation of cyclohexane is indicated by Hoot and Kobe [156]. In order of rising temperature of complete oxidation, the oxides which they studied are arranged as follows: copper chromite (170°C.), cobalt oxide (207°C.), ferric oxide (288°C.), silver oxide (292°C.), uranyl vanadate (294°C.).

In the case of Co-Mn spinels, a decisive influence on the catalytic properties in the oxidation reaction of propylene [150] is their structure. The activity of a spinel of the structure $Co^{2+}(Mn^{3+}Mn^{3+})O_4{}^{2+}$ is higher than that of $Co^{3+}(Mn^{2+}Co^{3+})O_4{}^{2-}$ because in the former there is an increase in the number of Mn cations, which can act as electron donors for the chemisorption of O_2 atoms better than Co cations can.

The high activity of spinel type catalysts has stimulated the study of their properties in the reaction of complete oxidation of hydrocarbons [58, 171, 172, 173] and the application of, for example, copper chromite to practical uses.

Table 24.

Oxidation of Isooctane (1.2-2.5%) in Air on Low-Percentage Catalysts on Asbestos at 7 x 10^3 hr^{-1}*

Catalyst	% of catalyst on carrier	Temperature of 50-60% conversion of isooctane to CO_2 and H_2O
Pt	0,1	213
Copper-chromium	2,0	300—325
Iron-chromium	3,0	300—350
Magnesium-chromium	3,0	350
Magnesium-silver	3,0	450—500
Iron-aluminum	3,0	Above 500
Copper-aluminum	3,0	Above 500

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*Table compiled on the basis of data from [97].

Of major interest are studies on the "modification" of spinels by admixtures of acids and certain salts of alkali and alkaline earth metals. L. Ya. Margolis et al. [138-140] showed the modifying effect of boric and hydrofluoric acids, barium sulfate and nitrate, and sodium silicate on copper and magnesium chromites. They noted that upon introduction of 2-5% of these compounds, the activity of spinels in the reaction of complete oxidation of ethylene and isooctane increases sharply. The "modification" of contacts affects the quality of the surface, occasionally altering the individual steps of the process.

Compounds with unsaturated (acetylenic, ethylenic) bonds oxidize readily on spinels (cobaltides) and mixed oxides (hopcalites) at relatively high space velocities, 21-60 x 10 hr^{-1} [92-94, 96, 99, 111]. Promoting of manganese-containing oxide catalysts with silver oxide and their deposition on a carrier (manganese ore, clay [116]) increase the stability of these contacts to the action of water vapor and to sintering, and their strength. Pyrolusite manganese ore activated with 1% silver oxide [92-94, 99] is used in the production of inert gases for the removal of acetylene from the oxygen-argon mixture.

In the preparation of manganese-containing oxide catalysts, a considerable importance is assumed by the method of precipitation, which affects the modification of manganese dioxide and its dispersity. Thus, in [149], α- and β-modifications of manganese dioxide, prepared by different methods, differed substantially in their activities in the oxidation reaction of carbon monoxide, probably because of different degrees of their dispersity. As was noted by the authors (who studied the formation of an amalgam and the reaction with copper oxide with the formation of an active contact), this was manifested by a difference in their chemical properties.

In [148], the activity of the initial α- and β modifications of MnO_2 was found to be similar. A difference in their behavior was displayed after promoting MnO_2 with silver oxide. Using x-ray structural analysis, the authors were able to establish that silver oxide was formed in large quantity on the surface of β-MnO_2, whereas on α-MnO_2 silver is converted mainly to silver manganite. The activity of the promoted catalyst in the latter case decreases and approaches that of the original manganese dioxide.

Among other spinel catalysts, a complete oxidation of organic compounds takes place at high rates in the presence of cobalt cobaltide. It is noted that its activity is similar to that of platinum and palladium catalysts.

Andersen et al. [142], who studied the oxidation of methane (at space velocities of 480 hr^{-1}) in air on 26 catalysts showed that the oxidation rate constants decrease in the following series of contacts: Pd/γ-Al_2O_3, Co_3O_4 - spinel, Co_3O_4 - mullite/γ-Al_2O_3, Pt/γ-Al_2O_3, Pd/γ-Al_2O_3, Cr_2O_3/γ- Al_2O_3, Mn_2O_3/γ-Al_2O_3 (Fig. 40). The temperature of complete oxidation of methane on Pd/Al_2O_3 is 300°C., on Pt/Al_2O_3 400°C., and on Co_2O_3/γ-Al_2O_3 500°C. Very similar results were obtained by oxidizing methane in oxygen on the same contacts (without a carrier) in [472].

The catalysts Co_3O_4 and Pd/Al_2O_3 are more suited for hydrocarbons which oxidize more easily: 2-pentene and benzene oxidize completely on these catalysts at 200°C. On platinum catalyst on aluminum oxide, the temperature of complete oxidation of these hydrocarbons is 50-100°C. higher.

In a study of the oxidation of methane (0.7-4%) in oxygen in a flow-through circulating unit (circulation rate 550 l/hr) over oxides of transition metals of the fourth period, G. K. Boreskov et al. [147] showed that cobaltous-cobaltic oxide displays the maximum activity. The reaction rate constant for the oxidation of methane (1%) at 300°C. (for some metals the value of K was obtained by extrapolating to 300°C. and 1% methane) decreases in the series: Co_3O_4, NiO, MnO, CuO, Cr_2O_3, Fe_2O_3, TiO_2 (Fig. 41). An analogous activity series of metal oxides was obtained by Boreskov et al. [151] in a study of the oxidation reaction of H_2 and isotopic and homomolecular exchange of O_2.

By comparing the activity of a series of oxides in oxidation reactions with the binding energy between oxygen and the surface of the oxides, determined by dissociating a part of the oxides, it was found that there is an inverse proportionality between the catalytic activity and the energy binding oxygen to the oxide surface [186]. The relationship found by Boreskov et al. provides a rational explanation for the data reported in the literature on the activity of transition metal oxides in oxidation reactions and offers new means of scientific selection of oxidation catalysts.

A relationship of this kind had been indicated earlier by Rienäcker in a study of the activity of a series of oxides in the oxidation reaction of carbon monoxide [174]. He showed that the catalytic activity of metal oxides in this reaction goes through a maximum when the oxides are arranged according to the binding energy. Oxides with a very high and very low oxygen-oxide binding energy are not suited for this reaction. In order for the oxidation reaction of carbon monoxide to proceed at the maximum rate, a certain optimum binding energy between oxygen and the surface of the oxides is required.

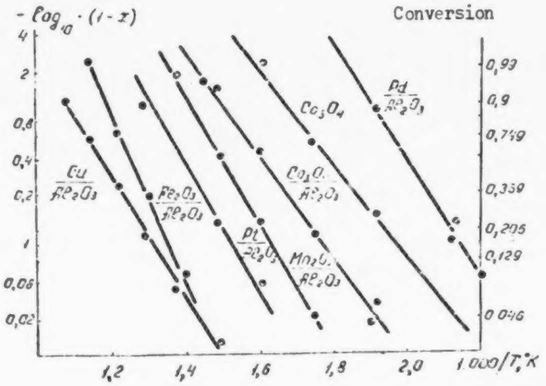

Fig. 40. Catalytic oxidation of methane at a space velocity of 380 hr^{-1} [142].

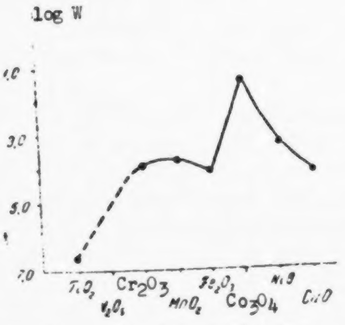

Fig. 41. Oxidation of 1% methane in oxygen at 300°C. over oxides of transition metals of period 4 [147].

Data from a number of studies indicate favorable prospects for the use of cobalt oxide catalysts for the removal of hydrocarbons from oxygen-containing gas mixtures. The cobalt catalyst Co_3O_4/Al_2O_3 oxidizes 93% of the hydrocarbons in exhaust gases [152]. The authors of the latter study noted that after 950 hours of service, the oxidation of the hydrocarbons was down to 87%. When cobalt catalysts are promoted with silver, they can be used for the removal of saturated and unsaturated C_2-C_4 hydrocarbons from gas mixtures at space velocities of 20 x 10^3 hr^{-1}, low temperatures (100°C.), and high pressures (P = 50-300 atm) [107, 108].

When cobalt catalysts are tested on carriers (silica gel, aluminum oxide, alumino-silicate) at a high temperature, the effect of interaction of cobalt oxide with aluminum oxide with the formation of the spinel $CoAl_2O_4$ is observed, the activity of this spinel being much less than that of cobalt cobaltide [142]. The inconsistency of data on the stability of the cobalt oxide catalyst on carriers may be due to the presence of different modifications of cobalt oxides.

The lack of reliable literature data on the stability of most oxide catalysts hinders their practical application in reactions of complete oxidation of hydrocarbons. More definite data are available on the use of Mn-pyrolusite ores promoted with oxides of silver and copper [92-94, 175] in processes of oxidation of acetylenic compounds, and on the use of copper-chromium catalyst for the purification of gaseous discharges of certain industrial organic processes [171, 172, 173].

Platinum and palladium catalysts, whose activity is largely determined by the method of preparation, conditions of activation, and chemical nature and structure of the carriers, are suitable for the complete oxidation of cyclic compounds, which are the most difficult to oxidize.

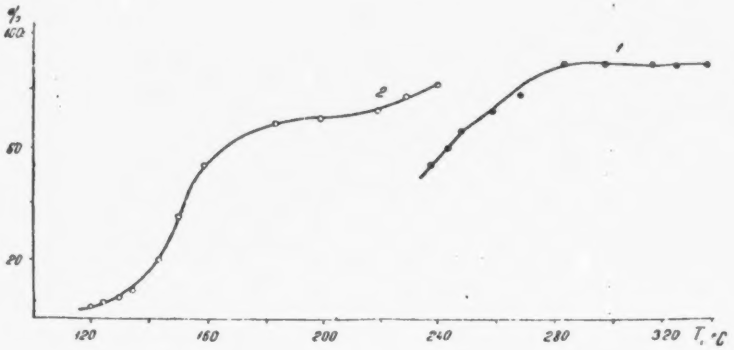

Fig. 42. Oxidation of 0.5% cyclohexane (1) and a mixture of 0.5% cyclohexane and 1% CO (2) in air over palladium catalyst on aluminosilicate at a space velocity of 6 x 10^3 hr^{-1}.

Fig. 42* shows data on the oxidation of cyclohexane (0.5 vol. %) and its mixture with 1% CO in air at a space velocity of 6 x 10^3 hr^{-1}. It is evident from the figure that a 90% oxidation of cyclohexane to CO_2 and H_2O is achieved at 280-300°C. both in the case of 0.5% cyclohexane and its mixture with 1% CO. Increasing the space velocity during the oxidation of cyclohexane to 12 x 10^3 hr^{-1} slightly decreases the activity of palladium catalyst: an 85% oxidation of the hydrocarbon is achieved at 330°C.

The oxidation of saturated hydrocarbons (for example, 1% of a propane-butane mixture in air) takes place at a high rate on platinum catalyst (0.5 wt. % Pt) [57]. The activity of platinum-palladium and other catalysts under comparable conditions proved lower than on platinum, as in the case of the oxidation of formaldehyde (Fig. 43).

Platinum-palladium catalyst on aluminum oxide (ΣMe = 1%) is used for analyzing mixtures containing methane [103]. At a space velocity of 36 x 10^3 hr^{-1} at 500°C., a 96-100% oxidation of the mixture to CO_2 and H_2O is achieved on this contact. On palladium catalyst, a complete oxidation of methane in a mixture with air is achieved at lower space velocities (450 hr^{-1}) and higher temperatures: 20% at 500°C., 80% at 750°C., and 100% at 800°C. [141].

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*Data of GIAP (State Institute of the Nitrogen Industry) obtained by oxidizing cyclohexane on palladium catalyst prepared at the Institute of Chemical Sciences of the Kazakh Academy of Sciences.

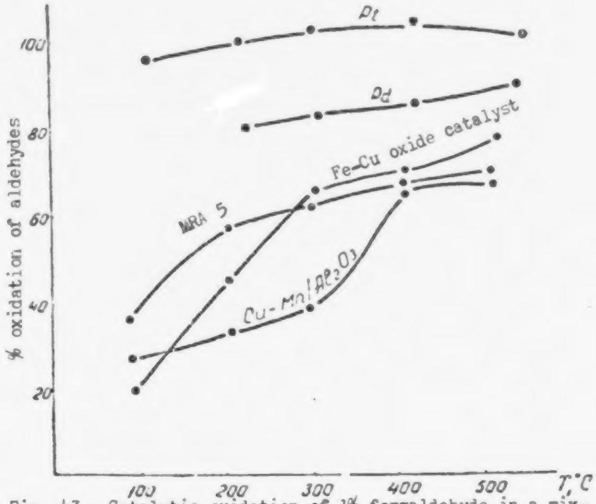

Fig. 43. Catalytic oxidation of 1% formaldehyde in a mixture with air at a space velocity of 36 x 10^3 hr^{-1}.

Platinum catalyst of domestic manufacture [105] is successfully used at space velocities up to 3 x 10^3 hr^{-1} for the oxidation of waste gas from plants producing synthetic fatty acids. At 300-350°C., the odor of toxic compounds is completely eliminated. Platinum catalysts on ceramic rods called "oxicats" [104], on aluminum oxide [105] and as an alloy with nickel [100] are used abroad for these purposes (judging from reports in the literature). These catalysts in the form of beads, screens, and metal plates purify waste gases from petroleum-cracking plants, [104], synthetic fatty acid production [105], coffee roasting, polymer factories [136], kitchen fumes, etc. The cost of catalytic devices operating at 250°C. is 1.5 greater than that of installing thermal combustion of the discharges. However, the operating cost of catalytic devices is 2.5 times lower because of a sharp reduction in the amount of fuel consumed by heating the components undergoing oxidation [102]. The service life of such units amounts to 2.5-6 thousand hours [104].

A number of schemes for the catalytic oxidation of organic impurities in the waste gases of chemical plants have been proposed in the literature. The use of catalysts in the form of screens and streamlined lattices decreases the resistance to the gas flow and permits an increase of the space velocities. According to the data of [137], in 1964, there were around 800 operating units for the catalytic purification of waste gases in Europe, and around 900 units in the entire world, operating on all-metal catalysts. However, the literature does not specify the service life of all metal catalysts, noting only that the alloy deteriorates rapidly when large amounts of acids and solid inorganic substances are present in the gas [101].

In recent years, a considerable amount of patent material has been published dealing with methods of purification of exhaust gases and preparation of catalysts for these purposes. Major attention has been given to the study of catalysts for the oxidation of hydrocarbons and CO in the exhaust gases of motor transport: chromites, molybdates, supported manganates [176], manganese-chromium catalyst [177], and contacts consisting of a mixture of chromite of nickel or cobalt deposited on Al_2O_3 coated with manganese oxide [178], or a mixture of oxides of cobalt and cerium [181], or oxides of cobalt, nickel (1-75 wt. %) and thorium (5-25%) [180].

Of interest are patents [106, 182] on the complete oxidation of methane. A series of platinum group catalysts and silver on aluminum oxide are proposed for this purpose. The reaction rate decreases in the following series of catalysts: rhodium, palladium, iridium, ruthenium, platinum, silver [182]. At 400-500°C., a complete oxidation of methane (1.5%) is observed in a mixture of 3% O_2 and 95.5% N_2 at a space velocity of 0.1-200 hr^{-1}. To purify the exhaust gases, platinum and palladium catalysts are combined wtih oxides of other metals [179, 183, 184]. Platinum or palladium are taken in amounts of 0.01 to 1% of the weight of the carrier; the oxide of the metal (for example, copper or vanadium), in amounts of 0.1 to 10.0%, the carrier constituting the balance. Admixtures of phosphorus salts or acids [184] and also compounds of sodium, lead, chromium and lanthanides in the form of salt solutions increase the stability of the contacts to poisons and the activity at relatively low temperatures.

An original solution to the optimum arrangement of catalysts is proposed in one of the British patents [185]. To lower the temperature of complete oxidation of hydrocarbons and CO in the exhaust gas, the authors separate the catalyst into two beds. At the entrance is placed a bed with the smaller volume (2-10% of the total volume) containing 0.5% platinum or palladium on aluminum oxide. The second bed sometimes contains no platinum (or contains 0.01% of it) and consists of the carrier and copper oxide on γ-Al_2O_3. The oxidation begins at a relatively low temperature in the first, thin bed. The distribution of the platinum over the beds lowers the temperature of the start of oxidation of the hydrocarbons and CO by 100°C.

Chapter 5

CATALYTIC REMOVAL OF NITROGEN OXIDES FROM EXHAUST GASES

The chief source of formation of nitrogen oxides in air are plants producing nitric acid and nitrogen fertilizers and the exhaust gases of motor transport. The content of nitrogen oxides in nitrous gases depends on the technological conditions and amounts to an average of 0.1-0.5 vol. % at most plants after absorption purification. The content of nitrogen oxides in "residual" gases must not exceed 0.1 vol. % if the air is to be diluted down to the sanitary levels (in the streets down to 0.1 mg/m^3, and in industrial buildings down to 5.0 mg/m^3). It is known from the literature [2] that the concentration of nitrogen oxides in areas adjacent to chemical plants and also on heavily traveled city streets is many times greater than the permitted level. The formation of smog, attributed by scientists to the reactions of nitrogen oxides with hydrocarbons under the influence of ultraviolet light, is a menace to the inhabitants of Los Angeles, San Francisco and other cities with a heavy automobile traffic. Thus, the removal of nitrogen oxides from atmospheric air and waste gases is a pressing problem whose solution will improve the sanitary working conditions and reduce unproductive losses of nitric acid.

Among the methods which may decrease the concentration of nitrogen oxides in gas mixtures, two should be mentioned: absorption and catalytic purification.

The process of absorption purification involves the absorption of nitrogen oxides by a volume of sorbent and in some cases a chemical reaction with solid or liquid absorbers. Various materials [448, 449, 455, 456] have been used as adsorbents at low temperatures, the most interesting of which may be aluminosilicates, zeolites, silica gels [455, 265, 282], and also iron and manganese ores [431, 432]. The use of solid absorbers may considerably decrease the volume of the units as compared with the volume of liquid purification devices, and reduce the investment in the removal of nitrogen oxides from exhaust gases. However, absorption by liquid and solid sorbents has many disadvantages which prevent its broad practical application. The absorption and chemical binding of nitrogen oxides with sorbents constitute a low-temperature process; raising the temperature substantially decreases their efficiency. The absorbing capacity of the sorbents is limited by the pore volume, and decreases in the presence of moisture and after high-temperature regeneration in the majority of the cases studied.

The thermal decomposition of nitrogen oxides, in particular NO to O_2 and N_2, takes place at a high temperature (600-1900°C.) and is accelerated in the presence of catalysts. Fraser and Daniels, who studied the decomposition process $2NO \rightarrow N_2 + O_2$ in an inert atmosphere (10% NO) at

700-1400°C. showed that the reaction rate depends on the nature of the oxide [439]. On aluminum oxide, the decomposition rate was two orders of magnitude higher than on other oxides, for example ZrO_2. The authors account for this fact by a variable adsorptive capacity of the oxides for NO: Al_2O_3, 1.3 x 10^{10}*; La_2O_3, 0.77 x 10^8; ZrO_2, 2.5 x 10^8; CaO, 0.96 x 10^9; ZnO, 1.1 x 10^8.

On transition metal oxides, the catalytic decomposition of NO and NO_2 takes place at lower temperatures.

Sourirayan and Blumenthal [473] note that in the presence of copper oxide on silica gel (3:7) at a space velocity of 1320 hr^{-1}, the decomposition of NO in nitrogen is already 69% at 510°C. The catalyst displayed on high stability (300 hours in overheatings to 1000°C.) and was used to remove nitrogen oxides from the exhaust gases of a two-cylinder engine operating on ethyl gasoline. In the latter case it is pointed out that copper oxide was reduced to the metal, and the process apparently proceeded via reduction of nitrogen oxide by the hydrogen and carbon monoxide present in the exhaust gas. Nitrogen dioxide in the presence of copper oxide and cerium oxide on Al_2O_3 (1:1) is 99% decomposed to NO, N_2, and O_2, and already 55% decomposed to $N_2 + O_2$ at 520°C. [445]. The process of decomposition of NO_2 is affected by the nature of the catalyst: at temperatures below 520°C., copper oxide is more active, and above this temperature, cerium oxide contact is (cf. Fig. 44). The addition of O_2 to the reacting inert mixture slightly decreases the percent decomposition of nitrogen oxides; for example, their decomposition in air at 520°C. occurs to the extent of 47% as compared to nitrogen (55%). Wikstrom and Nobe showed that the process takes place in two steps:

$$NO_2 \rightarrow NO + {}^1/_2O_2$$
$$NO_2 \rightarrow N_2 + {}^1/_2O_2$$

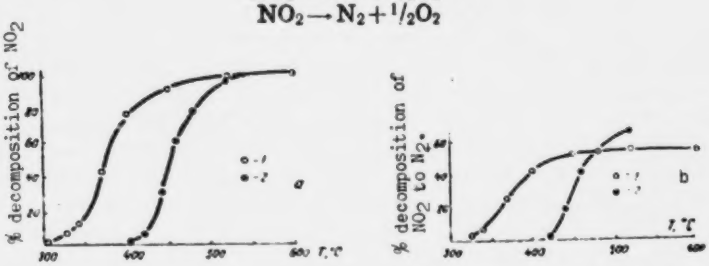

Fig. 44. Catalytic decomposition of NO_2 to nitrogen in an inert atmosphere over copper oxide (a) and cerium oxide (b) on aluminum oxide [445].

A study of the second step, the decomposition of NO to N_2 in a vacuum, was made by G. K. Boreskov et al. [457]. They showed that the catalytic decomposition of NO occurs at relatively low temperatures, 200-500°C., and the reaction rate decreases in the following series of contacts: Co_3O_4, CuO, NiO, Fe_2O_3, Cr_2O_3, ZnO. The temperature at which a similar specific activity of the oxides at P_{NO} = 200 mm Hg is observed increases in this series.

Expressed in number of molecules per cm^2.

Oxide	$W_{sp}\ \frac{\text{mole NO}}{\text{m}^2\text{, min}}$	Temperature, °C.
Co_3O_4	3.1×10^{-8}	275
Fe_2O_3	2.3×10^{-8}	355
Cr_2O_3	3.0×10^{-8}	450

The reaction rate increases in proportion to the square of the NO concentration, and as a result, the authors postulated that as the concentration of nitrogen oxide in oxygen-containing exhaust gases decreases, the reaction rate should be moderate.

A second-order reaction with respect to nitric oxide was also observed in [447], where the decomposition of nitric oxide (0.40-0.43 vol. %) was carried out in nitrogen in the presence of platinum-nickel catalyst at 500-625°C. The decomposition reaction of nitric oxide occurs at the rate $W = \frac{A \cdot (P_{NO})^2}{1 + \beta \sqrt{P_{O_2}}}$, i. e., is inhibited by adsorbed oxygen formed in the course of the reaction.

In order to facilitate the desorption of oxygen from the surface of the catalysts and give the reaction a different course, reducing gases are employed. In some cases, at a high content of the reducing gas and an oxygen concentration up to 3-4%, this makes it possible to carry out the process of reduction of nitrogen oxides to nitrogen, water and ammonia at high space velocities. Thus, it is noted in [459] that the rate of reduction of nitric oxide by hydrogen is 850 times faster than in an inert atmosphere.

The reducing agents used for the removal of nitrogen oxides from inert and oxygen-containing gaseous media are hydrogen [443, 444, 452, 458, 459, 475], methane [443, 451], carbon monoxide [438, 441, 446, 460, 475], hydrocarbons [436], ammonia [435, 437, 474], natural gas [433], and cyanamide [478]. Basic data on these studies, performed for the most part during the last decade, are listed in Table 25. It is evident that in the majority of the studies, the concentration of nitrogen oxides was close to their content in the effluent gases of nitric acid plants or exhaust gases of internal combustion engines. We shall consider studies in which the reduction of nitrogen oxides was carried out in inert media. Schwab and Drikos [477] investigated the reduction of N_2O by carbon monoxide on a catalyst at different concentrations of the components. They showed that the reaction rate increases sharply starting at 250-300°C., is proportional to the nitric oxide concentration in the mixture when ther is an excess of carbon monoxide, and proportional to the carbon monoxide concentration in excess nitrous oxide. In an excess of the reducing gas, metallic copper acts as the catalyst, and in the presence of excess nitrogen oxides, copper oxide is formed, and the rate of the reaction is limited by the process of its reduction (E = 23 kcal/mole).

A systematic study of the reduction of nitrogen oxide by hydrogen and carbon monoxide was made by Sourirayan and Blumenthal over a prereduced copper catalyst on silicon oxide [475]. The authors found that the degree of interaction is determined by the composition of the gaseous mixture and reaches 90-100%, starting at a ratio of nitrogen oxides to hydrogen of 1:1 and to carbon monoxide of 1:3 at 250°C. (see Fig. 45, which we plotted by using the data of [475]). An increase of the space velocity to 12×10^3 hr^{-1} in the presence of a 5-10-fold excess of carbon monoxide, hydrogen or their mixtures practically did not decrease the degree of removal of nitrogen oxides. The presence of hydrocarbons in the mixture had a positive effect. The introduction of oxygen into the mixture with a large excess of reducing agent did not affect the reaction. Analysis of the reduction products showed that depending on the conditions, nitrogen oxides are reduced by hydrogen to nitrogen and ammonia.

This was also observed by Aven and Peters [444], who studied the reduction of nitric oxide [pressure 0.005-0.05 atm at 375-425°C. over a copper-zinc-chromium oxide catalyst (29% Zn, 10% Cu, 31% Cr)].

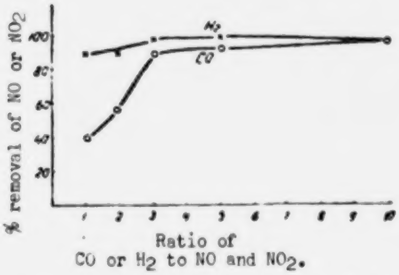

Fig. 45. Reduction of nitrogen oxides by hydrogen and carbon monoxide over copper oxide on silica gel at 250°C. [475].

The process of reduction of nitric oxide to ammonia is limited by the step of hydrogen activation. The rate of reduction to nitrogen increases in proportion to the concentration of the initial components (NO and H_2). In the case of silver catalyst, the rate of reduction of nitrogen oxides by hydrogen (taking place at 60-180°C. with formation of water) is also proportional to the hydrogen pressure [452]. It is postulated that the first stage is the decomposition of nitrogen oxides to the elements, whereupon hydrogen reacts with the adsorbed oxygen.

Excess hydrogen in the reacting mixture ($NO:H_2 = 1:250$) promotes the reduction of nitrogen oxides to ammonia. In the reduction of NO by hydrogen over platinum and rhodium catalysts on aluminum oxide [476, 458], by using spectroscopic and gas chromatographic analyses of the reacting mixture at different temperatures, Kokes observed that the reaction takes place via the formation of N_2O, whose content in the mixture increases sharply at 260°C. (Fig. 46).

One of the products of the reduction of nitrogen oxides in hydrogen is water, which does not have a negative influence in the case of platinum and silver catalysts. Something different is observed in the reduction of nitrous oxide in the presence of aluminum oxide. In this case, the water formed in the reaction decreases both the amount and rate of adsorption of both components on the surface [459]. The reaction rate in this case is expressed by the equation $W = \frac{k_1 P_{N_2O}^{1/2} \cdot P_{H_2}^{n_2}}{1 + k_2 P_{H_2O}}$, where $n_2 = 0.33-0.66$.

Nitrous oxide is an intermediate in the reduction of nitric oxide to nitrogen by carbon monoxide. This process was studied by Shelef and Otto [460] over transition metal oxides and platinum on aluminosilicate in a slight excess of carbon monoxide (1.2 moles of CO and 2 moles of NO). The maximum of formation of nitrous oxide is observed in a certain temperature interval characteristic of each catalyst: Fe_2O_3 (200°C.), $CuCr_2O_4$ (180°C.), CuO (220°C.), Cr_2O_3 (240°C.), NiO (300°C.), Pt (300°C.), Co_3O_4 (350°C.), and aluminosilicate (460°C.). No nitrous oxide is formed over MnO and V_2O_5.

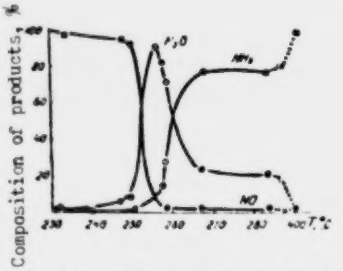

Fig. 46. Effect of temperature on the composition of the products in the reduction of NO by hydrogen [458].

From Fig. 47 (borrowed from [480]), which shows the results for ferric oxide on aluminosilicate (10% Fe_2O_3), it is evident that in the case of ferric oxide catalyst, the maximum quantity of nitrous oxide is formed at 200°C., and at higher temperatures it is reduced by carbon monoxide to nitrogen. The content of carbon monoxide decreases as the reaction temperature is raised, and that of carbon dioxide increases, since the latter results from the reaction of both nitrogen oxides with carbon monoxide. A shift of the maxima of nitrous oxide formation toward higher temperatures over a series of contacts indicates a decrease of their activity in this reaction.

The data obtained in the present study on the mechanism of reduction of nitric oxide by carbon monoxide were confirmed by Baker and Doer [446], who studied this process on a copper-chromium catalyst without a carrier. The stepwise course of the reaction and the lag at the stage of formation of nitrous oxide are attributed by the authors to a strong adsorption of the reaction product, carbon dioxide, at low temperatures (below 160°C.). At higher temperatures, the reduction of nitric oxide to nitrogen occurs smoothly since carbon dioxide is not adsorbed on the catalyst. At 200-270°C., the degree of removal of nitrogen oxides from inert gas mixtures by means of carbon monoxide amounts to 70-90% at space velocities of the gas streams up to 36 x 10^3 hr^{-1} (Fig. 48). These results indicate a real possibility of removing nitrogen oxides from inert gases by means of reducing agents. The rate of reduction of nitrogen oxides under these conditions is limited by the activation of the initial components, whose concentration ratio and temperature determine the nature of the end products (N_2O, N_2, H_2O, NH_3, CO_2) and their influence on the kinetic characteristics of the process. Another important factor is the nature of the catalyst that specifically adsorbs the starting, intermediate, and end products, and determines the reduction temperature.

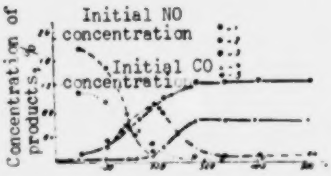

Fig. 47. Change in the composition of gas mixture during reaction of NO with carbon monoxide over Fe_2O_3/aluminosilicate (10% Fe_2O_3) at different temperatures [460]. 1 - CO_2; 2 - NO; 3 - N_2O; 4 - N_2; 5 - CO

A considerable excess of the reducing agent is used to reduce nitrogen oxides in oxygen-containing gas mixtures. Thus, in the study of Roth and Doer [441], 0.4% NO was quantitiatively reduced at a content of 6 vol. % carbon monoxide. The introduction of oxygen into the composition of the gas mixture changes the degree of removal of nitric oxide as well as carbon monoxide from this mixture. If in the adsence of oxygen (cf. Fig. 49, a and b) nitric oxide is completely reduced by carbon monoxide, and the latter is removed to an insignificant extent, the situation changes when oxygen is introduced. The percent oxidation of carbon monoxide is directly proportional to the amount of oxygen introduced; at a close to atoichiometric oxygen concentration, it reaches 100%. The degree of removal of nitric oxide from the mixture remains high (100%) at a carbon monoxide content exceeding the stoichiometric amounts relative to oxygen, then decreases as a result of deficiency of the reducing agent. Apparently, at a carbon monoxide concentration exceeding that which is necessary for complete reaction with oxygen and NO, the surface is coated with carbon monoxide. The reaction proceeds as a result of the interaction of adsorbed carbon monoxide with oxygen and NO molecules striking the surface and thus becoming instantly activated. When the oxygen concentration exceeds the stoichiometric quantities, oxygen is preferentially adsorbed on the surface, thus decreasing the possibility of adsorption of NO. When there is an insufficient quantity of carbon monoxide and activated NO molecules, the reaction of catalytic reduction of NO by carbon monoxide is depressed.

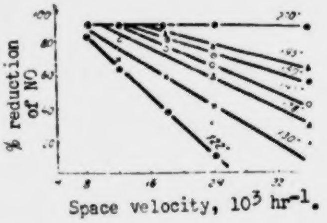

Fig. 48. Reduction of NO by carbon monoxide in an inert atmosphere on copper-chromium contact as the temperature and space velocity change [446].

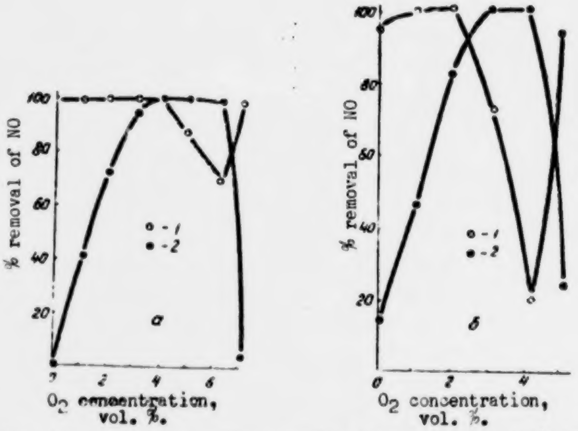

Fig. 49. Effect of oxygen concentration on the percentage of removal of nitric oxide (1) and carbon monoxide (2) from gas mixtures at 250°C. and a space velocity of 10 x 10^3 hr^{-1}: a - over barium-promoted copper chromite; b - over copper chromite on aluminum oxide (6.8% CuO, 6.8% Cr_2O_3) [441].

On the basis of the data cited by Doer and Roth [441], one can compare a series of tested catalysts used for the reduction of nitrogen oxides by carbon monoxide in the presence or absence of oxygen in gas mixtures. It is evident from Table 25 that when oxygen is absent from the mixture, the reduction of nitric oxide is fairly complete at low temperatures. Even at 245°C., in the presence of barium-promoted copper chromite and copper oxide on aluminum oxide (3.4 wt. %), the percent age of reduction is 100. When oxygen is introduced into the composition of the mixture, barium-promoted copper chromite is the most active catalyst.

Roth and Doer [441] point out that the degree of removal of nitric oxide from a gas mixture increases with the carbon monoxide concentration. This is also noted by Sokol'skiy and Alekseyeva [113, 395], who studied the purification of the exhaust gas of a two-stroke engine in the presence of 16.8-17.3% O_2 over unactivated manganese ore (see Table 25). As the carbon monoxide concentration in the initial mixture increases from 2.5 to 5.6%, for a similar content of nitrogen oxides, the degree of removal of the latter and carbon monoxide increases. The results cited in [113, 441] are of practical interest, since the gas mixtures from which toxic components are removed are close in composition to the actual compositions of the exhaust gases of internal combustion engines.

Additional data on the removal of nitrogen oxides from oxygen-containing gas mixtures can be found in the patent literature. A survey of a few patents in this area shows that the process as carried out in industry consists of two stages [143, 451]. In the first stage, excess, higher-than-stoichiometric amounts of hydrogen, methane or natural gas are introduced into the mixture to be purified in order to make them react with oxygen and form carbon dioxide and water. In the second stage, the excess reducing gas reacts with the nitrogen oxides. The temperature of the process is determined chiefly by the nature of the reducing gas. When hydrogen is used, the reaction takes place at 150-200°C., and in the case of ammonia at 150-250°C., whereas methane requires a higher temperature (400-430°C.). Because the first stage of the reaction is exothermic a heating-up of the catalyst is observed which increases in proportion to the oxygen content of the mixture. In the case of catalysts, mainly precious metals of group 8 are used: platinum, palladium, rhodium, ruthenium [433, 434, 436, 464], palladium-ruthenium [48. 68, 440] and their mixtures on carriers (aluminum oxide, ceramics, etc.).

Andersen et al. [434, 435, 437, 464] showed that the process of reduction of nitrogen oxide is considerably facilitated when the reducing agents used are ammonia (stoichiometric amounts relative to nitrogen oxides) or methane in high concentrations (up to 57%). The removal of nitrogen oxides from oxygen-containing gas mixtures can then be accomplished in a single stage at high space velocities (60-200 x 10^3 hr^{-1}) at temperatures of 125-550°C. A selective reduction (of nitrogen oxides only) by ammonia according to the equations

$$2NH_3 + 3NO \rightarrow {}^5/_2 N_2 + 3H_2O$$

$$4NH_3 + 3NO_2 \rightarrow 3{}^1/_2 N_2 + 6H_2O$$

Table 25.

Catalytic Removal of Nitrogen Oxides from Exhaust Gases.

Catalyst, Composition	Composition of Gases, Concentration of nitrogen oxides	Space Velocity, hr^{-1}	Temperature, °C.	Degree, % of Purification	Characteristics of Catalysts and Process	Reference
1	2	3	4	5	6	7
Pt, Pd, Ru, Ir, Ag, Rh and Pd + Rh on aluminum oxide (0.5 wt. % metal)	Nitrous gases: 0.1-0.5 vol. % nitrogen oxides, plus added methane, natural gas, 3-21% O_2	—	365-415 (not above 760)	—	For mixtures with 3% O_2, Rh/Al_2O_3 (~450°), and for those with 21% O_2, Pd/Al_2O_3 (~450°) are recommended	[433]
Pd/Al_2O_3	Nitrous gases: 0.1-0.5% nitrogen oxides, 3-4% O_2 + 1.6% methane + water vapor, nitrogen	$20-200\cdot10^3$	100-600, optimum 300-350	—	Removal of nitrogen oxides is carried out after removing H_2, CO and hydrocarbons. Reaction occurs satisfactorily with 30-70% excess methane over the reaction with nitrogen oxides and oxygen	[434]
Pt, Pd, Ru, Rh, Ir, Ag and their mixtures on aluminum oxide	Nitrous gases: tenths of one percent of nitrogen oxides and a few percent of O_2 + NH_3	—	—	—	Nitrogen oxides reduced in two stages: 1. $2NO+2NH_3 \xrightarrow[150-400^\circ]{Pt} 3H_2O+2N_2$ 2. H_2 or CH_4 is added to the remaining nitrogen oxides, and the reaction is carried out at 150-900° over Pt, Pd on Al_2O_3 or aluminosilicate	[435] [435]

Pt/carrier	0.3% nitrogen oxides, 3% O_2, H_2O - 0.8%, stoichiometric quantity of NH_3 for the reaction with nitrogen oxides	60—90	150—250	90—98 %	Ammonia reacts only with nitrogen oxides, catalyst stable for three months (labor[illegible] data). Process acc[illegible]plished in one stage.	[464]
Ni, Pt, Pd on aluminum oxide	Nitrogen oxides in waste gases of chemical plants. Natural gas or hydrocarbons with H_2 are added, P = 0.035 kg/cm²	25—150·10³	450—1100	—	Temperature of chemical reductant controlled by introducing inert gases into the reaction space	[436]
Co, Fe, Ni on aluminum oxide (5-6% metals)	22% O_2, 2% NO + 2% NO_2 + 8% H_2O + ammonia and inert gases	до 20·10³	200—300 (Ni, CO) 160—250 (Fe)	92—99 50—80	—	[437]
APC-2 + dunite	Waste gases from production of nitric acid. Addition of carbon monoxide present in gases emitted from plants of cuprammonium purification, 2-5% O_2, 0.2% CO	24—41·10³ (Linear 1.7-2.7% l/min hr-1 Gas volume 77-131 m³	260—470 Over the catalyst 705—810 (Past the catalyst)	85—100	—	[438]
Pd-Ru on aluminum oxide	Converted gas (nitrogen oxides 0.2-1.0 cm³/m³, H_2 70-71%, acetylene, O_2 0.1-0.3%	Catalyst volume 10·10³	150—160	95—96	Catalyst operated stably for 6.5 months	[68, 440, 264]
Unactivated manganese ore	Exhaust gases of two-stroke internal combustion engine, laboratory data 16,8—17,8% O_2, 0,0014—	19·10³	100 200 300 400 500	0—14,5 57—70 52—62 47—62 26—39	Percent removal of nitrogen oxides from exhaust gas increases with increasing CO content of mixture	[118]

Continuation of Table 25

1	2	3	4	5	6	7
	0,0013% NO, 0,0088—0,0032 1—3% CO_2, 2,5—5,6% CO					
Copper chromite	6% CO+0,4% NO+N_2	$10\cdot10^3$	242	69	—	[441]
Copper chromite	6% CO+0,4% NO+3O_2+N_2	*	249	26	—	
Copper chromite promoted with barium	6% CO+0,4% NO+N_2	*	245	100	—	*
	6% CO+0,4% NO+N_2	*	215	77	—	
CuO—Cr_2O_3/Al_2O_3 (3,4% CuO, 3,4% Cr_2O_3)	6% CO+0,4% NO++4% O_2+N_2	*	245	100	—	
	6% CO+0,4% NO+N_2	*	245	83	—	*
	6% CO+0,4% NO++3% O_2+N_2	*	246	35	—	
CuO/Al_2O_3 (3,4% CuO)	6% CO+0,4% NO+N_2	*	242	100	—	
	6% CO+0,4% NO+N_2	*	245	93	—	
	6% CO+0,4% NO+N_2	*	200	91	—	
CuO—Cr_2O_3/Al_2O_3 (6,8% CuO, 6,8% Cr_2O_3)	6% CO+0,4% NO+N_2	*	164	78	—	*
	6% CO+0,4% NO+N_2	*	105	32	—	
	6% CO+0,4% NO++N_2+2,0% O_2	*	245	100	—	
Pt on nichrome (80% Ni,/20% Cr)	0,3—0,5% Nitrogen oxides 1—4% O_2, N_2	$120\cdot10^3$	400—580	Complete purification	Maximum allowed overheatings up to 1500°, catalysts operate for 2-3 hours	[442]
Pt/Al_2O_3, ceramic	0,3—0,5% Nitrogen oxides N_2+H_2, 2—4% O_2	30—50$\cdot10^3$	150—200	—		
	0,3—0,5% Nitrogen oxides+ N_2 +CH_4+2—4%	*	400—430	—		[443]
CuO—ZnO—Cr_2O_3 (10% Cu, 29% Zn, 31% Cr)	Nitrogen oxides NO +H_2 in N_2(NO:H_2=1:1) P==0,005—0,05 atm	2000 ml/min	375—425	—	Rate increases with concentrations of reacting gases	[444]

Continuation of Table 25

CuO/Al_2O_3 (1:1)	NO_2 in nitrogen, 1260 ppm	10—77,8 ml/sec	350	25	—	[445]
			400	40		
			520	55		
CeO_2/Al_2O_3 (1:1)	»	»	450	20	—	[445]
			460	40		
			550	60		
Plant $CuO-Cr_2O_3$ (17% Cr_2O_3, 82% CuO)	NO, 1500 ppm +1%CO+N_2	$16 \cdot 10^3$	200	90	—	[446]
		»	160	80		
		»	138	75		
		»	130	65		
		»	122	40		
		$24 \cdot 10^3$	195	78		
		$36 \cdot 10^3$	195	65		
Ni—Pt/Al_2O_3 (0,1% Pt, 3%Ni)	0.40–0.43% nitrogen oxides, in nitrogen, P = 1.15 atm	—	500—625	—	—	[447]
Pd cn spherical carrier (0.5% Pd)	0.3% nitrogen oxides 3,0—4,0% O_2, H_2O, N_2+ +CH_4	$33 \cdot 10^3$	451	8 ppm ($NO + NO_2$) in purified gas	—	
		$66 \cdot 10^3$	485	14 ppm	—	[464]
		$120 \cdot 10^3$	405	650 ppm	—	
»	0,3% Nitrogen oxides 3—4% O_2+65% H_2, 10% CH_4, N_2	$57 \cdot 10^3$	549	128 ppm	—	[464]
»	0,3% Nitrogen oxides 3—4% O_2, 40% CO, 15% H_2 6% CH_4	$60 \cdot 10^3$	526	15 ppm	—	[464]

Continuation of Table 25

1	2	3	4	5	6	7
	0.3% nitrogen oxides, 3-4% O_2, 20-26% CH_4, and other hydrocarbons + N_2 are added	$57,6 \cdot 10^3$	396	51 ppm	—	[464]
Pd on spherical carrier (0.5% Pd)	0,3% Nitrogen oxides, 3—4% O_2, H_2+N_2	$66—68 \cdot 10^3$	150—163	5—9 ppm	—	[464]
CuO/SiO_2 (3:7)	892 ppm NO in nitrogen	1320	510	69	In the laboratory, the catalyst was stable for 300 hours, and in the stream of exhaust gas of a two-stroke engine, for 5100 hours	
CuO/SiO_2 (3:7)	400-800 ppm NO, 550-1400 ppm NO_2 + carbon monoxide, hydrogen (ratio of nitrogen oxides to gas reductant was varied from 1 to 10).	2000—10000	300	100 in the presence of excess gas reductant		[473] [475]
3% Ni+2% Cu on grog	NO—0,3%, O_2—2,7%, N_2+Ar—97%. Amount of H_2 is 2-3 times larger than the stoichiometric value	600—800 m^3/hr, P = 3-4 atm	500—550	Residual NO content 0.0007%	The catalyst was tested for 3 months and was stable during service.	[461, 462]

can be carried out on platinum, palladium, ruthenium, cobalt, and nickel, although the authors prefer the platinum contact. In the presence of this catalyst, ammonia being added (1 mole of ammonia per mole of nitrogen oxides and 10 moles of oxygen) to the gas mixture to be purified, nitrogen oxides are almost completely removed (up to 10 ppm of nitrogen oxide by weight remains) (Fig. 50). The selective reaction of ammonia with nitrogen oxides is attributed by the authors of [464] to the low rate of reduction of oxygen under these conditions

$$2NH_3 + 1^1/_2O_2 \rightarrow N_2 + 3H_2O.$$

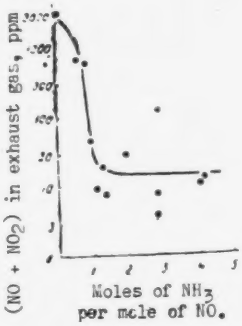

Fig. 50. Effect of ammonia concentration on the content of nitrogen oxides in the mixture after their reduction at 150-200°C. (NO$_2$ + NO - 0.28-0.30%, O$_2$ - 3.0-3.4%) [464].

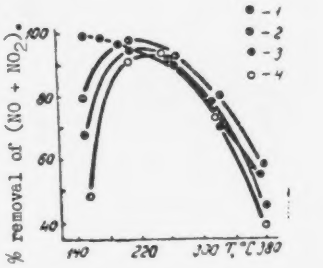

Fig. 51. Effect of temperature and space velocity on the percentage of selective reduction of nitrogen oxides (0.3%) by ammonia over platinum in an oxygen-containing gas mixture (3% O$_2$) [464]. 1 - 10 x 10^3 hr^{-1}; 2 - 30 x 10^3 hr^{-1}; 3 - 60 x 10^3 hr^{-1}; 4 - 90 x 10^3 hr^{-1}.

Of interest are data obtained by these authors on the effect of temperature and space velocity on the catalytic reduction of nitrogen oxides by ammonia over 0.57 platinum on a carrier [464]. From Fig. 51 it is evident that at space velocities of 60-90 x 10^3 hr^{-1} at temperatures as low as 150-250°C. the degree of removal of nitrogen oxide from the gases amounts to 90-98%. At lower temperatures, the process is inhibited by the adsorption of ammonium nitrates and other salts being formed on the catalyst.

Judging from the papers [465-469] and the survey [463], the catalytic purification of waste gases of nitric acid plants is widely employed in foreign practice. Depending on the natural resources, the reductants used are methane and natural gas, and in areas where these are lacking, ammonia.

Soviet researchers have used APK-2 platinum catalyst to remove nitrogen oxides from the waste gases of nitric acid production [438]. The reducing gas used was carbon monoxide from gases of a cuprammonium purification column. The platinum catalyst operates with a high efficiency at space velocities of 14-27 x 10^3 hr^{-1} and a degree of purification of 75-92% (Table 26).

Table 26.

Decomposition of Nitrogen Oxides of Waste Gases from the Production of Nitric Acid in an Experimental Unit [438].

Gas Composition: 2.6-5% O_2, 0.2% CO + Nitrogen Oxides

Gas Volume, m^3	Space Velocity, 10^3 hr^{-1}	Temperature, °C.		Linear Velocity	Percent Removal of Nitrogen Oxides
		Over Catalyst	Past Reactor		
Two-bed catalyst (3.15 1) APK-2 + dunite					
77	24,4	415—470	725—810	1,74—1,9	100
112	35,6	260—415	505—710	1,87—2,36	99
131	41,5	260—391	405—705	1,88—2,71	85
Single-bed catalyst APK-2 (6.9 1).					
298,8	14,3	160—260	590—790	1,9 —2,3	92,5
123,4	17,9	165—220	580—730	2,3 —2,7	86,0
155	22,5	170—215	615—720	2,98—3,31	85,8
189	27,4	185—270	640—705	3,5 —3,76	75,4

The use of a two-bed catalyst (the second bed being dunite) makes it possible to increase the space velocities of the process to 41.5 x 10^3 hr^{-1} and the percentage of purification to 85-100% with a certain decrease of the total volumes of purified gases (lower linear velocity). A two-layer contact is proposed by the authors for gases with a high oxygen content.

Of major interest are data on the reduction of nitrogen oxides in oxygen-containing mixtures in the presence of supported common metal catalysts [442, 437, 463]. Figure 52, plotted on the basis of Andersen and Keith's patent description [437] shows the temperature dependence of the percent reduction of nitrogen oxides by ammonia in the presence of reduced cobalt, nickel and iron catalysts on aluminum oxide (5-6% metals) at a space velocity of 20 x 10^3 hr^{-1}. It is evident that at 200-275°C., the nickel and cobalt catalysts display the maximum activity. In their presence, nitrogen oxides are 90-100% reduced by ammonia at a high oxygen content (22%). Iron catalyst is active at a lower temperature: at 165°C., the percent reduction of nitrogen oxides is close to 80%.

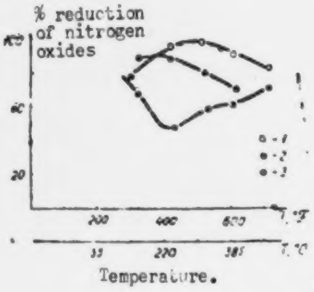

Fig. 52. Reduction of nitrogen oxides (2% NO, 2% NO_2) by ammonia in oxygen-containing mixtures at a space velocity of 20 x 10^3 hr^{-1} over cobalt (1), nickel (2), and iron (3) catalysts on aluminum oxide (5-6% Me) [437].

According to the data of Fletcher [442, 443] and British patents, a nickel-chromium alloy catalyst (80% Ni, 20% Cr) promoted with platinum is suitable for the removal of nitrogen oxides from gases at an oxygen content of 1-4.3%, space velocity up to 120 x 10^3 hr^{-1}, and temperature of 400-580°C. Reduced platinized and chromized nickel foil and nickel-chromium catalyst were used to remove nitrogen oxides from gases by reduction with methane (natural gas) in [80, 81]. The authors showed that at 500-600°C. a complete reduction of nitrogen oxides on the nickel-chromium catalyst and chromized nickel foil takes place at a space velocity not above 14-15 x 10^3 hr^{-1} [81]. A low stability of the nickel-chromium plant catalyst was observed (50 hours as compared to 160-200 hours for chromized nickel foil). Platinizing of nickel foil increases the activity (complete purification at a space velocity of 28.6 x 10^3 hr^{-1}) and stability of the contacts.

To lower the temperature of the process, as recommended in a US patent (2910343), 27 October 1959), the authors of [80] used a two-bed catalyst. A bed of GIAP-3 palladium catalyst (0.16% Pd), whose volume amounted to 1/6 of the total volume of the contact, was placed above the chromized nickel foil catalyst. Under these conditions, it was possible to reduce the nitrogen oxides in the exhaust gas down to the sanitary permissible concentrations (30-40 m^3/hr) at 550°C. and a $CH_4:O_2$ ratio below the stoichiometric value (0.6), i. e., in an oxidizing atmosphere. A complete removal of nitrogen oxides is achieved at $CH_4:O_2 = 1.1$.

Over nickel catalyst with admixtures of copper on grog (3% nickel + 2% copper), nitrogen oxides were completely reduced by hydrogen (2-3-fold excess at 500-600°C. and a space velocity of 600 hr^{-1} [461, 462].

Despite the relatively high activity, common metal catalysts are unstable, particularly in the purification of actual exhaust gases, for example, from nitrogen fertilizer plants [453], and can operate only in the presence of a large excess of the reducing gas. For this reason, supported precious metal catalysts with metal contents of 1.8-2% and space velocities of 8 x 10^3 hr^{-1} are recommended for practical adoption by plants in the USSR, [453, 454]. The purification takes place in one stage at a high temperature and pressure, and the reducing gas is able to react with nitrogen oxides and oxygen. A method of high temperature purification has been developed for mixtures containing up to 3% oxygen. At a higher oxygen content, it is necessary to apply the two-stage scheme described above.

A pronounced effect in the high-temperature removal of oxides from oxygen-containing mixtures was observed by using combined [438, 80] and mixed catalysts [454], which make it possible to reduce the consumption of the precious metal. The method of preparation of a mixed palladium-ruthenium catalyst and the development of a method of removal of nitrogen oxides and acetylene from converted gas are reported by F. P. Ivanovskiy et al. [68, 440, 264]. The catalyst proposed by the authors is marked by a high activity in the reduction of nitrogen oxides in hydrogen-containing gas mixtures (excess hydrogen). The same contact may be successfully used to remove nitrogen oxides from exhaust gases of gasoline engines containing substantial amounts of carbon monoxide and hydrogen under most operating conditions.

Chapter 6

BENCH AND ROAD TESTS OF EXHAUST PURIFICATION CATALYSTS

Laboratory tests of catalysts for oxidizing carbon monoxide and other components of exhaust gases on artificial mixtures are the first and indispensable steps in the selection of catalysts. A second important step consists in testing optimum catalysts on the actual gas of internal combustion engines mounted on benches. Bench tests proposed in the USSR for catalysts used for purifying the exhaust gases of gasoline engines have been conducted on a model installation at the Central Scientific Research and Experimental Design Laboratories of Neutralizers and Automobile and Tractor Power Engineering. The design of the installation and the procedure for testing and analyzing the mixtures, discussed in [70], made it possible to determine the efficiency of catalysts as a function of temperature (100-500°C.), space velocity of the gas flow (20-120 x 10^3 hr^{-1}), and carbon monoxide concentration (up to 6% CO).

A series of catalysts supplied by various organizations were tested: platinum (0.2%) and manganese-copper oxide catalysts on aluminum oxide (Karpov Physicochemical Institute, Moscow), copper-chromium oxide catalyst (Azizbekov Institute of Petroleum Chemistry, Baku), copper oxide-activated iron ore (NIOGAZ, Moscow), palladium catalyst (0.5-0.75% palladium), platinum-palladium catalyst (0.25-0.5 wt. % total metals) on aluminum oxide, and iron-copper oxide on clay (Institute of Chemical Sciences, Kazakh Academy of Sciences).

Bench tests were carried out on catalysts having a high activity, stability, and thermal stability under laboratory conditions on artificial mixtures [54, 56-62, 71]. Figure 53, based on data of LANE [70], illustrates data comparing the efficiency of the action of these catalysts in the oxidation of 1% carbon monoxide as the temperature of the exhaust gas of the "Moskvich-407" engine changed (space velocity 33-38 x 10^3 hr^{-1}).* The air injection amounted to 30% of the total gas flow.

As is evident from this figure, the degree of oxidation of carbon monoxide is substantially determined by the temperature and chemical composition of the catalysts. At 100-200°C., the degree of oxidation is low, and at 200-220°C. it ranges from 5 to 35%, depending on the catalyst. The maximum activity at 220°C. was displayed by platinum and palladium catalysts on carriers and activated siderite. As the temperature rises in the presence of these contacts, the degree of oxidation increases sharply and reaches 100% for platinum and palladium at 320-340°C., and in the case of copper oxide-activated iron ore, at 400°C. The platinum-palladium catalyst is also characterized by a sharp increase in activity as the temperature changes from 240 to 270°C.; a complete oxidation of carbon monoxide is observed at 380°C.

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* A mixture of 4.5–6% CO and 7% O_2 was oxidized on the platinum catalyst.

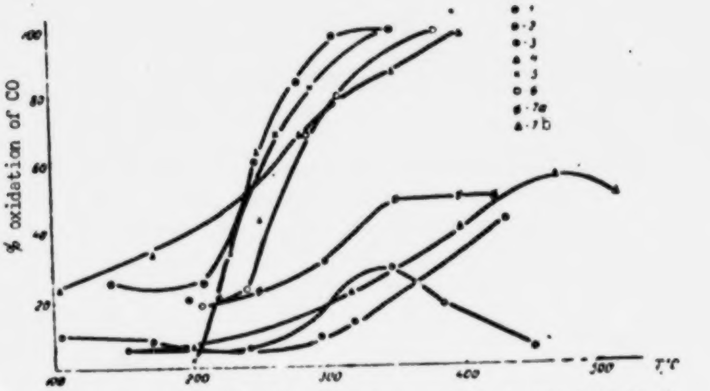

Fig. 53. Catalytic oxidation of carbon monoxide in the exhaust of MZMA-407 engine (space velocity 33-38 x 10^3 hr^{-1}) as the temperature of the gas changes [61, 70]: 1 - Pt/Al_2O_3 (0.24% Pt); 2 - CuO-MnO_2/Al_2O_3 (CuO:MnO_2 = 2:3, Σ oxides 15 wt. %); 3 - CuO-Cr_2O_3 (3:2); 4 - CuO-activated siderite; 5 - Pd/aluminosilicate (0.5 wt. % Pd); 6 - Pt-Pd aluminosilicate (0.5 wt. % Σ Me); 7 - Fe_2O_3, CuO/clay, Fe:Cu = 4:1 (atomic); Σ oxides : carrier = 1:2; 7 a - calcined sample; 7 b - uncalcined sample.

The activity of oxide catalysts increases slowly with rising temperature and reaches a maximum, 50-55%, for the iron-copper oxide catalyst on clay at 350-450°C., 40% for the manganese-copper oxide catalyst on aluminum oxide at 420°C., and 30% for the copper-chromium catalyst at 350°C. A further temperature elevation decreased the activity of the iron-copper oxide and copper-chromium catalysts, apparently either because of a change in the phase composition of the catalysts under the influence of the reacting mixture, or as a result of poisoning by some impurities, for example, water vapor, which may have a poisoning effect.

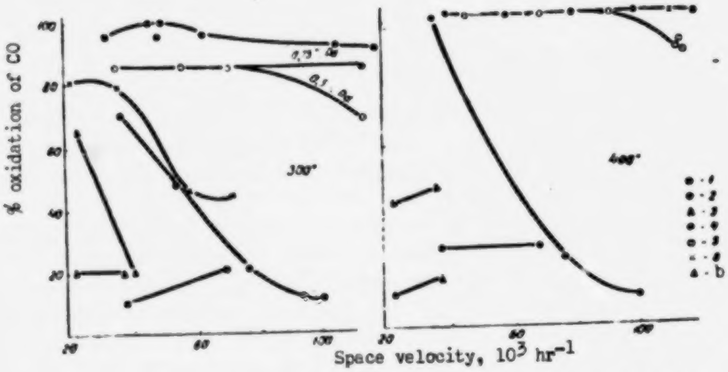

Fig. 54. Effect of space velocities on the catalytic oxidation of carbon monoxide in the exhaust of MZMA-407 engine at 300°C. (a) and 400°C. (b)[70, 61]. Notation same as in the preceding figure.

In view of the fact that the volume of exhaust gases changes with different operating conditions of the engines, the effect of contact time on the efficiency of oxidation of carbon monoxide was investigated. A space velocity of 20-120 x 10^3 hr^{-1} was achieved by varying the volume of the catalyst. The efficiency of the catalysts at 300 and 400°C. at various space velocities is illustrated in Fig. 54, a and b. The experiments showed that as the space velocity increases at 300°C., there is a sharp decrease in the degree of oxidation of carbon monoxide to 20% at space velocities of 40-80 x 10^3 hr^{-1} in the presence of activated siderite and iron-copper oxide catalysts. There is also observed a decrease in the activity of platinum-palladium contact to 45% at 60-79 thousand 1/1 of catalyst per hour.

Platinum and palladium catalysts on carriers behave differently. The degree of oxidation of carbon monoxide over platinum contact as the space velocity is raised to 120 x 10^3 hr^{-1} varies between 90 and 100%, over palladium catalyst with 0.75% palladium it amounts to 85%, and decreases to 70% when the palladium content is lowered to 0.5 wt. %. At 400°C., with a wide variation of the space velocities of the gas flow, the degree of oxidation of carbon monoxide over platinum, palladium and platinum-palladium catalysts is 100% and decreases by 10-15% only at 114 x 10^3 hr^{-1} over palladium catalyst. Raising the temperature had no positive effect on the activity of siderite. Oxide catalysts at space velocities of 20-70 x 10^3 hr^{-1} were relatively insensitive to the contact time, and their activity remained as high as before.

In order to study the effect of carbon monoxide concentration in the exhaust gas, a series of experiments were carried out at a space velocity of 40 x 10^3 hr^{-1} over palladium catalyst on bead aluminosilicate (0.5 wt. % Pd) with preheating of the gas before the reactor to 286°C. Figure 55 shows the change in percent oxidation of carbon monoxide, the temperature in the reactor and past it, and the oxygen content in the exhaust gas before and past the reactor as the carbon monoxide content in the exhaust gas increased from 0.2 to 6 vol. %. It is evident that as the carbon monoxide concentration increases, the oxygen content in the exhaust gas past the catalyst decreases from 6 to 2%. The extent of oxidation of carbon monoxide depends on its concentration: whereas at 0.2-2.0 vol. % CO it amounts to 50%, at 2.5-3.0 vol. % it increases to 100%, at 4% to 90%, and at 5.7% it drops to 65% because of the insufficiency of oxygen on the surface. Because of the liberation of a large amount of heat by the oxidation of carbon monoxide and hydrocarbons, the temperature within the catalyst rises, and at a carbon monoxide concentration of about 6% reaches 795°C. Thus, starting at 200°C. (10-20%), palladium catalyst achieves a fairly complete oxidation of carbon monoxide over a wide range of space velocities and CO concentrations in the exhaust gas, and at 340°C. all of the carbon monoxide is eliminated.

In addition to the above-indicated contacts in the experimental gas purifier, LANE (0.5 1) tested mixed palladium-copper, palladium-iron and palladium-

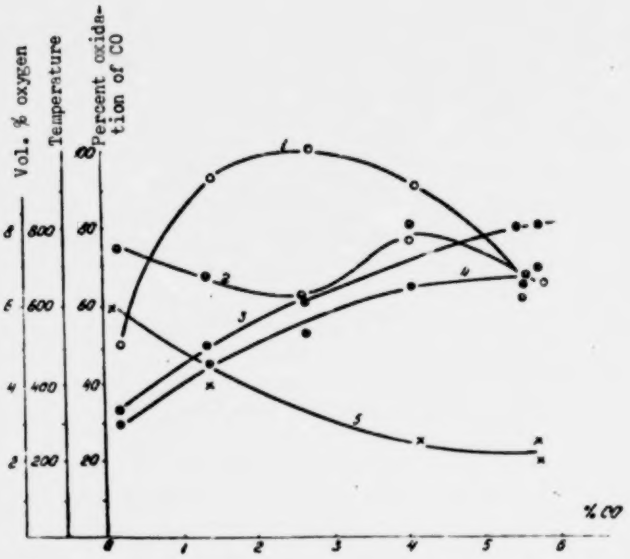

Fig. 55. Effect of carbon monoxide concentration in the exhaust of "Moskvich-407" engine at 36×10^3 hr^{-1} on the efficiency of palladium catalyst (the gas being preheated to 200°C.) [70, 61]. 1 - percent oxidation of carbon monoxide; 2 - oxygen content of exhaust gas, vol. %; 3 - temperature of catalyst; 4 - temperature of exhaust gas past the catalyst; 5 - oxygen content past the gas purifier, vol. %.

cobalt contacts on aluminosilicate (Table 27). During the tests, the rotational speed of the crankshaft (1500-2500 rpm) and the fuel feed were varied, the temperature was measured before and after the gas purifier, and the gases were analyzed chromatographically for the content of carbon monoxide, carbon dioxide, oxygen, and hydrogen before and after purification in the exhaust gas of the "Moskvich-407" engine. (The gases were preheated to 400°C. during the purification.) It is obvious from the data obtained that when the carbon monoxide content of the engine exhaust was 3-5 vol. % and the hydrogen content up to 1.0-1.8 vol. % (leaned-out mixture) over mixed palladium catalysts at 1500 rpm, the degree of removal of carbon monoxide S ranges from 0.79 to 0.97. As the speed during operation of the engine on the leaned-out mixture is increased to 2500 over the palladium-cobalt catalyst, S decreases to 0.69, over palladium-iron to 0.89, and over palladium-copper to 0.5. The average degree of purification in operation on the leaned-out mixture is 0.7, and the purification of the gas over palladium-cobalt catalyst is better. The composition of the exhaust gas past the gas purifier includes 3-7 vol. % oxygen and 9-10% carbon dioxide. Hydrogen, which is present in the exhaust gas in the case of the leaned-out mixture, is completely oxidized over the catalyst and obviously the first to undergo oxidation. From the oxygen content of the gas past the gas purifier one can infer that the concentrations of the reacting components on the surface of the catalyst are very similar.

During the operation of an engine on an enriched mixture, the composition of the exhaust gas includes a large amount of carbon monoxide (7-14 vol. %) and hydrogen (2.8-4.9 vol. %), and the degree of removal of carbon monoxide decreases sharply, apparently because of a deficiency of oxygen on the surface of the contacts: the composition of the gas past the gas purifier contains 2.6-4.0 vol. % O_2. In this case, it is evident that carbon monoxide, hydrogen and hydrocarbons (whose analysis was not performed) are primarily adsorbed on the surface of the catalyst, hindering the activation of oxygen.

As is evident from an analysis of the bench tests of a series of catalysts, the best catalysts from the standpoint of removal of carbon monoxide from gasoline engine exhausts are supported platinum and palladium catalysts, which have shown a high efficiency over a wide range of space velocities (up to 114 x 10^3 hr^{-1}) and gas temperatures, starting at 250°C. and above. In the case of palladium catalysts in the presence of a high carbon monoxide and hydrogen content, the degree of oxidation varies as a result of an insufficient suction of air (1/3 of the gas flow) through the injector.

LANE conducted comparative bench and experimental road tests of platinum and palladium catalysts in the exhaust gases of the MZMA-407 engine in KNG-150 and KNG-450A neutralizers on the ZIL-130 truck (Table 28, 29). It is apparent that in the degree of removal of CO from the exhaust gas of the ZIL-130 engine, palladium catalyst is identical to platinum. In the case of the MZMA-407 engine in a KNG-150 gas purifier at 1500 rpm, the degree of purification at all loads is 10-20% lower than on platinum catalyst.

Some catalysts were tested for the purification of diesel engine exhausts: bench tests were conducted in a gas purifier designed by GIPRouglegormash (State Experimental Institute of Design and Construction for the Coal-Machinery and Mining Industries) (KDM-100 four-cylinder engine), and road tests were carried out in a thermocatalytic gas purifier designed by S. S. Filatov [72] in collaboration with LANE and the Mining Institute (Sverdlovsk).

Bench tests with the KDM-100 four-cylinder diesel engine were conducted on palladium and platinum-palladium catalysts on synthetic aluminosilicate (0.5 wt. % metals on the carrier)* and on an iron-copper oxide contact on clay (iron-copper = 4:1, Σ oxides : carrier = 1:2). The catalyst (10 l) was placed in a shelf-type gas purifier. The exhaust gas before the catalyst passed through a bed of aluminosilicate which partially removed water, soot and other impurities. During the tests, the gas temperature in the catalyst bed was measured, and the gas was analyzed before and past the gas purifier for its content of carbon monoxide, aldehydes, nitrogen oxides, and carbon dioxide.

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* The tests were conducted in the heat engineering laboratory of the GIPRouglegormash Institute.

Table 27

Oxidation of Carbon Monoxide and Hydrogen in the Exhaust Gas of "Moskvich-407" Engine in the Presence of Mixed Palladium Catalysts (Total Metals 0.75 wt. %, 0.5 1) in an Experimental Gas Purifier Designed by LANE

Catalysts	Speed, rpm	Fuel Feed	Gas Temperature, °C		CO		CO_2		O_2		H_2		Injection Coefficient	Degree of Purification S
			I	II	I	II	I	II	I	II	I	II		
Palladium Copper	1500	Leaned-out mixture	560	620	5,0	0,23	9,2	11,0	3,5	3,5	1,8		0,34	0,97
		Enriched	450	450	10,14	9—12	3—6	3,6	4,0	5,0	4,8	4,0	0,14	0—0,07
	2000	Leaned-out	510	460	0,05	0,02	9,7	9,5	6,8	6,1	0,0	0,0	0,02	0,49
		Enriched	410	460	13,7	12,7	4,1	4,3	3,5	4,3	4,6	4,5	0,01	0,02
	2500	Leaned-out	576	610	2,4	1,1	10,1	10,0	4,2	3,8	0,95	0,0	0,08	0,5
		Enriched	510	560	10,0	9,8	6,5	5,0	4,5	5,3	4,9	2,6	0,12	0,0
Palladium Iron	1500	Leaned-out	490	520	3,0	0,17	9,75	10,3	3,0	2,9	1,2	0,0	0,22	0,98
		Enriched	460	540	7,0	6,0	8,0	7,9	3,5	3,4	2,8	0,1	0,08	0,1
	2000	Leaned-out	520	520	0,17	0,12	9,5	10,9	3,6	3,6	0,65	0,0	0,0	0,3
		Enriched	480	490	11	10,5	5,5	4,9	2,6	3,0	3,8	3,4	0,06	0,05
	2500	Leaned-out	550	610	2,8	0,28	2,2	9,7	2,7	4,2	0,9	0,01	0,09	0,89
Palladium Cobalt	1500	Enriched	420	630	12,5	11,2	4,2	4,5	3,75	4,5	3,8	1,8	0,06	0,046
		Leaned-out	500	500	0,40	0,07	10,0	8,0	3,9	7,0	0,35	0,0	0,20	0,79
	2000	Enriched	430	560	12,0	10,0	4,7	4,5	3,2	6,2	4,00	2,7	0,18	0,056
	2500	Leaned-out	550	610	2,7	0,74	9,6	9,4	3,9	4,5	1,1	0,03	0,21	0,69

Note. Numeral I denotes the temperature and content of the components before the gas purifier, and numeral II, past the gas purifier.

Table 28

Laboratory-Road Tests of KNG-450A Neutralizer with Alumina-Platinum and Palladium (0.75 wt. % Pd) Catalysts on ZIL-130 Truck

Conditions of Motion		Alumina-Platinum Catalyst			Palladium Catalyst		
Speed, km/hr	Load, t	CO Content, %		% Purification	CO Content, %		% Purification
		Before Neutralizer	After Neutralizer		Before Neutralizer	After Neutralizer	
	—	5,0	0,10	98	10	0,25	97
30	2,5	1,0	0,10	90	1,75	0,10	94
50	2,5	0,40	0,07	83	0,50	0,05	90
70	2,5	0,75	0,15	80	0,45	0,11	75

Table 29

Tests of KNG-150 Neutralizer with Alumina-Platinum and Palladium Catalysts (0.75 wt. % Pd) in Exhaust Gases of MZMA-407 Engine

Operating Conditions of Engine		Alumina-Platinum Catalyst			Palladium Catalyst		
rpm	Load, %	CO Content, %		% Purification	CO Content, %		% Purification
		Before Neutralizer	After Neutralizer		Before Neutralizer	After Neutralizer	
1500	25	2,3	0	100	2,7	0,6	78
	50	2,5	0,1	96	2,4	0,5	79
	75	2,0	0	100	2,0	0,4	80
	100	5,9	1,0	83	1,0	0,3	70
2000	25	2,7	0,2	93	2,7	0,8	89
	50	2,6	0,3	89	3,0	0	100
	75	1,1	0,1	90	1,4	0,1	93

Figure 56 shows the change of the carbon monoxide content in the exhaust gas during its oxidation over platinum-palladium catalyst as a function of the engine load. As the latter increases, the amount of carbon monoxide in the initial exhaust gas increases, and at a load of 70-80% amounts to 0.018 vol. %. The oxidation causes a decrease in the carbon monoxide concentration on the catalyst at all loads. At a load of 40-50%, the degree of oxidation reaches 90%. At the same time, the carbon monoxide concentration in the exhaust gas is 0.0018 vol. %, which approaches the sanitary level of carbon monoxide for the air of industrial buildings (0.0016 vol. %).

Starting with a 40% engine load and above, the temperature in the catalyst bed rises to 220-470°C., this being apparently responsible for a 50% or higher completion of the oxidation reaction of carbon monoxide. A 60% removal of

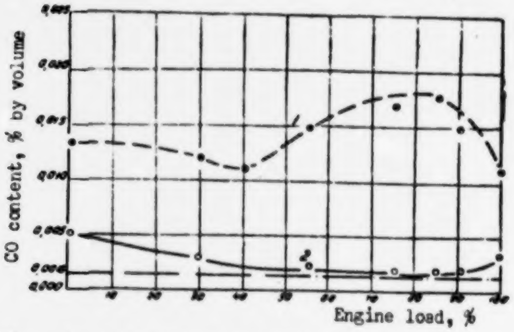

Fig. 56. Change of carbon monoxide content in the exhaust gas of KDM-100 engine at various loads in the presence of supported platinum-palladium catalyst: 1 - CO content (%) before gas purifier; 2 - past gas purifier

carbon monoxide from the exhaust gas during idling was obtained after warming up the engine under different conditions. Analysis of the gas showed that the content of nitrogen oxides past the catalyst does not change (0.00017 vol. %); no aldehydes were observed in the majority of the samples, owing to the incompleteness of the analytical procedure.

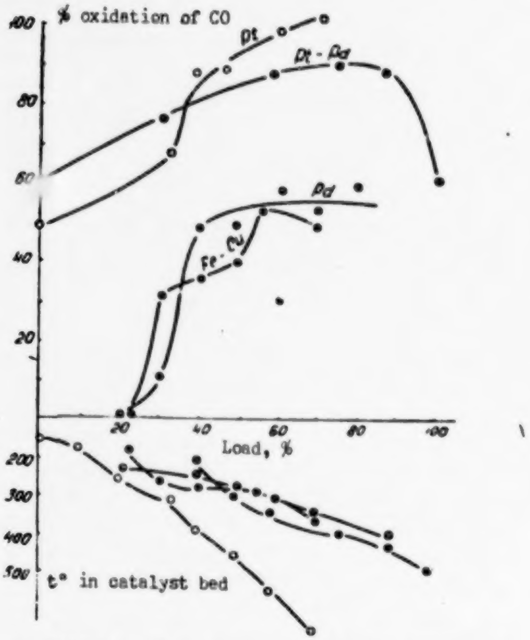

Fig. 57. Oxidation of carbon monoxide in the exhaust of KDM-100 diesel engine in the presence of platinum (Oxy-France) platinum-palladium, palladium and iron-copper oxide supported catalysts at different engine loads.

Tests of palladium catalyst in the same gas purifier showed that as the exhaust gas passes through the catalyst (initial carbon monoxide content 0.015-0.005 vol. %), the carbon monoxide concentration starting with a load of 40% and higher at a temperature of 250-400°C. decreases to 0.004-0.0023 vol. %. At a smaller engine load, because of a lower temperature in the catalyst (200°C. or lower), the oxidation proceeds less intensely.

In the course of extended tests of the catalysts on diesel engines stands, despite the use of aluminosilicate filters, the catalysts were coated with soot. A high activity of the contacts was maintained by periodically burning up the soot at 600°C. by passing air over them.

Figure 57 shows results of oxidation of carbon monoxide in the exhaust gas of a KDM-100 diesel engine as a function of the load in the presence of platinum-palladium, palladium, and iron-copper supported oxide catalysts and also platinum in a gas purifier made by Oxy-France Co. (the platinum catalyst was tested by R. M. Popovichenko [69]).

As is evident from the figure, the low-percentage palladium catalyst with a small admixture of platinum (25 at. %) on synthetic aluminosilicate is not inferior to the Oxy-France platinum catalyst in the degree of oxidation of carbon monoxide in the exhaust gas, particularly at small engine loads and during idling. However, the temperature in the platinum catalyst bed for the same load is 100°C. or higher than that in the platinum-palladium catalyst.

Palladium catalyst operating under less favorable temperature conditions showed poorer results because of a low carbon monoxide concentration. In order to increase the activity of palladium catalyst (0.35 wt. % Pd) in the shelf-type gas purifier, the exhaust gas of KDM-50 engine* was first heated to 500°C. Results of the tests showed (Fig. 58) that even during idling, the degree of removal of carbon monoxide from the exhaust gas amounts to 87%. With increasing engine load (50% and higher), the degree of oxidation of carbon monoxide reaches 90%.

Thus, platinum-palladium and also palladium (0.35-0.5 wt. %) and iron-copper oxide catalysts can be used to remove carbon monoxide from diesel engine exhaust gases with preheating of the latter.

The road tests for efficiency of palladium catalyst on aluminum oxide and other catalysts were carried out in an NTK-6M thermocatalytic gas purifier of Filatov's design at the Sokolovskiy quarry of the Sokolovskiy-Sarbay ore-dressing complex (May 1967). The gas purifiers (two) were installed on an MAZ-525 truck. The gas was preheated with a burner during the descent into the quarry and during loading of the truck at the face (with the engine idling).

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* Tests conducted on stand of KDM-50 engine of Volgograd Polytechnic Institute, catalyst volume 20 l.

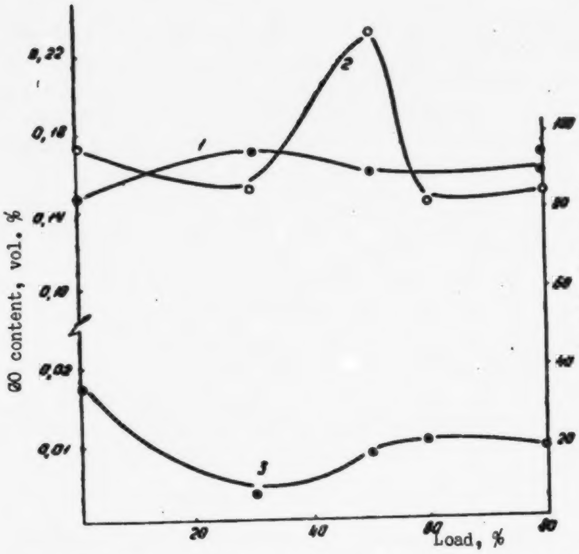

Fig. 58. Oxidation of CO in the exhaust gas of KDM-50 engine, the gas being preheated to 500°C. over Pd/aluminosilicate (20 l of 0.35% Pd) at different engine loads. 1 - degree of removal of CO from exhaust gas, %; 2, 3 - carbon monoxide content (in vol. %) before and past gas purifier.

Table 30

Road Tests of Palladium Catalyst on Aluminum Oxide (0.5 wt. % Pd)** on Diesel Engine of MAZ-525 Truck in NTK-6M Thermocatalytic Gas Purifier

Degree of Purification, %		
Carbon Monoxide	Aldehydes	Soot
Climb from Quarry, Load 25 t		
49	70	50
Descent into Quarry without Load		
72	100	40
Idling rpm while Standing Still		
79	58	50
Average Degree of Purification		
66	76	47

Table 30 lists data on the purification of the exhaust gas of the MAZ-525 dump truck in an NTK-6M thermocatalytic gas purifier with palladium catalyst (the figures listed are average arithmetic data of all the determinations under the indicated conditions based on records of the tests).

Palladium catalysts are characterized by an average oxidation of carbon monoxide of 66-69%, aldehydes 54-76%, and soot 36-47%. Thus, the efficiency of operation of the NTK-6M thermocatalytic gas purifier with the catalysts tested is above 50% for all the components. Since the catalyst operates in a thermocatalytic gas purifier in a fluidized bed, of major practical interest are tests of the catalysts for the duration and stability of operation under road conditions.

** Catalyst made by the Institute of Chemical Sciences, Kazakh Academy of Sciences.

Efficiency Road Tests of Palladium Catalysts for Purification of Gasoline Engine Exhaust Gases

In 1967, the Scientific Research and Experimental Design Laboratory of Neutralization and Truck and Tractor Power Engineering (KazNIPIAT) in collaboration with the Institute of Chemical Sciences, Kazakh Academy of Sciences, and other organizations carried out the first stage of official efficiency road tests on palladium and a number of other catalysts.

The catalytic oxidation of the toxic components of exhaust gases was carried out in gas purifiers whose design and theory of operation were developed primarily for platinum and palladium catalysts prepared at the Scientific Research and Experimental Design Laboratory of Neutralization and Automobile and Tractor Power Engineering [14, 73, 74]. The basic characteristics of the designs of the gas purifiers employed involve the use of bead catalysts in the form of a thin layer compressed between perforated screens, and an additional injection of air through an injector before the reactor to ensure an effective removal of carbon monoxide from the gas at a space velocity of 100×10^3 hr^{-1}. A diagram of the catalytic gas purifier is shown in Fig. 59.

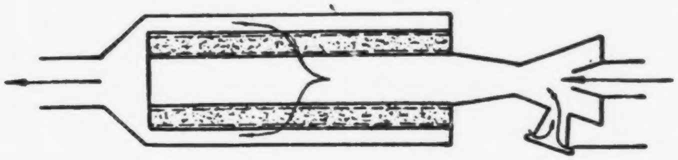

Fig. 59. Diagram of catalytic gas purifier for gasoline engine exhaust gases.

The toxicity of exhaust gases in the tested gas purifier design decreased as a result of two factors: dilution of the exhaust gas by the injected air (by approximately 1/4) and as a result of catalytic oxidation. The degree of catalytic purification S was calculated by allowing for the dilution. Results of chromatographic analysis (the sampling was duplicated) of the exhaust gases before and past the gas purifier (2-3 machines of each brand) were recorded.*

Tests of the catalytic gas purifiers were carried out on five types of gas purifiers according to a specially developed procedure under the conditions prevailing in Moscow, the Ust'-Kama gypsum mine, and Alma-Ata in motor vehicles of the models ZIL-585, ZIL-130, GAZ-51, GAZ-52, "Moskvich-408", M-21 and LAZ-585, with three vehicles of each of the models. The Chemistry Institute of

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* Chromatographic analysis of exhaust gases was carried out in specialized laboratories of LANE and KazNIPIAT.

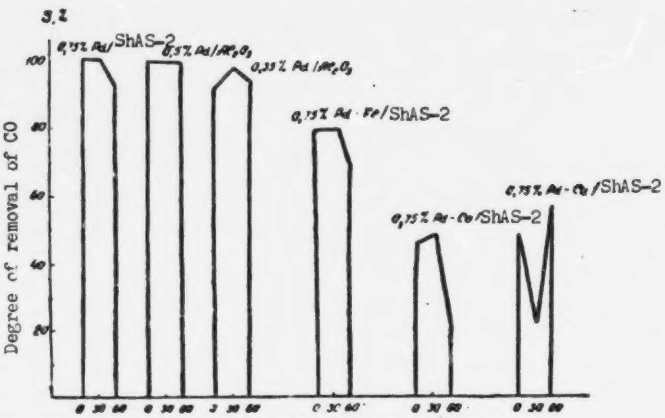

Fig. 60. Degree of removal of carbon monoxide from the exhaust gas of ZIL-130 engine in the presence of various catalysts at various catalysts at various traveling speeds under load.

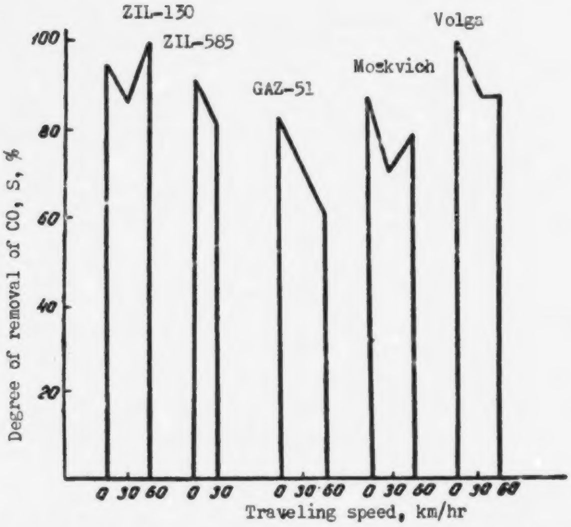

Fig. 61. Degree of removal of carbon monoxide from the exhaust gas of various engines under different conditions of motion in the presence of palladium catalyst on aluminum oxide (0.5 wt. % Pd) and aluminosilicate (0.75 wt. % Pd).

the Kazakh Academy of Sciences furnished experimental batches of palladium catalyst on bead aluminosilicate (0.75 wt. % palladium), on bead aluminum oxide (0.5, 0.35 wt. % palladium) and mixed catalysts on synthetic aluminosilicate (palladium-cobalt, palladium-copper, palladium-iron, palladium-nickel) for the tests, with a total metal content of 0.75 wt. %, which had shown positive results in bench tests at the LANE laboratory.

Results of tests of gas purifiers with palladium catalysts in Moscow and at the Ust'-Kama gypsum mine are considered below. Figure 60 presents data on the degree of removal of carbon monoxide from the exhaust of the ZIL-130 truck in the presence of various palladium catalysts under different conditions of motion under load. The traveling speed of the truck (in km/hr) is plotted along the horizontal axis, and the degree of catalytic removal of carbon monoxide from the gas (in %), allowing for dilution with air, along the vertical axis.

It is evident from Fig. 60 that the oxidation of carbon monoxide is substantial over all the catalysts except palladium-cobalt and palladium-copper on aluminosilicate. The carbon monoxide content of the exhaust gas during the purification decreases to 0-0.5 vol. %.

The most efficient catalyst from the standpoint of degree of removal of carbon monoxide from the exhaust gas is palladium on aluminum oxide (0.35-0.5% palladium) and on aluminosilicate (0.75 wt. % palladium). In their presence, carbon monoxide is practically completely oxidized under all conditions, and the degree of purification ranges from 65 to 80%, whereas over palladium-cobalt and palladium-copper catalysts on aluminosilicate, it amounts to less than 50%, and thus the carbon monoxide content at 30-60 km/hr remains high (~2%).

According to the degree of oxidation of carbon monoxide in the exhaust gas of ZIL-130 engine operating under load and without it, the catalysts tested may be arranged as follows: palladium on aluminum oxide (0.5 wt. % Pd), Pd/ShAS-2 (0.75 wt. % Pd), Pd/Al_2O_3 (0.35 wt. % Pd), Pd-Fe/ShAS-2 (0.75 wt. % Σ Me), Pd-Cu/ShAS-2 (0.75 wt. % Σ Me), and Pd-Co/ShAS-2 (0.75 wt. % Σ Me).

Figure 61 shows the results of oxidation of carbon monoxide in the exhaust gas of various engines (with and without load) in the presence of the best of the catalysts studied, at different traveling speeds and during idling.

Analysis of the exhaust gas before and past the gas purifiers with the catalysts Pd/ShAS-2 (0.75 wt. % Pd) and Pd/Al_2O_3 (0.5 % Pd), installed on GAZ-51, ZIL-130, "Volga", and ZIL-585 motor vehicles operating with and without load, showed that the degree of purification ranges from 85 to 100% during idling and at a traveling speed of 30-60 km/hr.

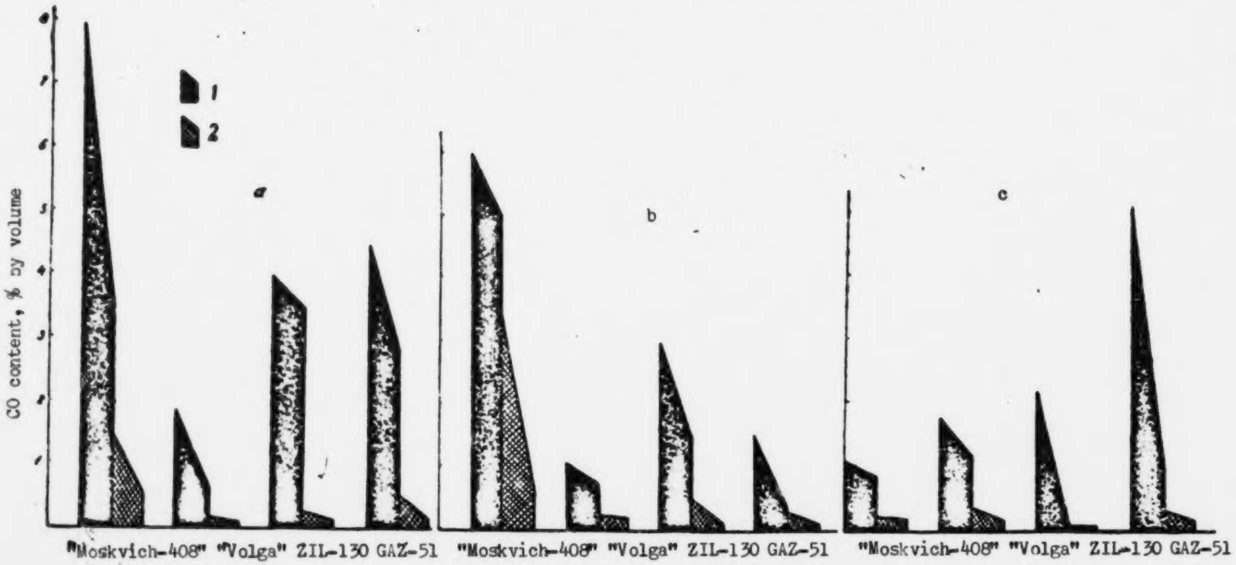

Fig. 62. Change of carbon monoxide concentration (1 - before, 2 - after purification) in the exhaust gases of various engines during their motion under load in the course of purification over palladium catalyst on aluminum oxide (0.5 wt. % Pd) and aluminosilicate (0.75 wt. % Pd). a - idling; b - speed 30 km/hr; c - 60 km/hr.

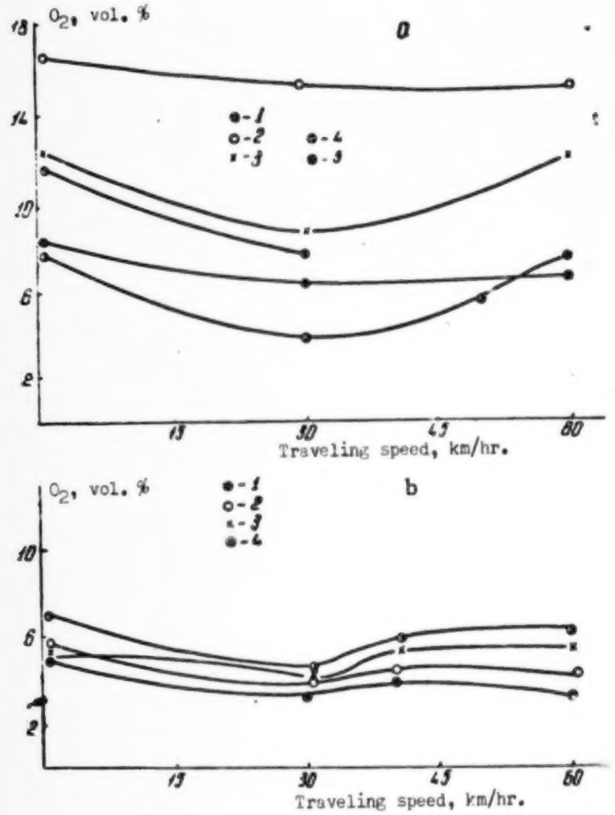

Fig. 63. Average oxygen content in the exhaust gas past the gas purifier; a - under Moscow conditions: 1 - "Moskvich-408"; 2 - ZIL-585; 3 - "Volga"; 4 - GAZ-51; 5 - ZIL-130; b - under Alma-Ata conditions: 1 - "Moskvich-408"; 2 - GAZ-52; 3 - ZIL-585; 4 - PAZ-652.

The greatest effect of purification and maximum reduction of carbon monoxide content under all conditions of motion is achieved (Fig. 62) in the purification of the exhaust gas from engines of ZIL-130 and "Volga" apparently because of the lower CO concentration in the initial exhaust gas than in the other engines.

A different picture is observed in the testing of palladium catalysts on "Moskvich" automobiles (city taxicabs). The carbon monoxide concentration in the exhaust gas of the "Moskvich-408" engine at 30 km/hr and during idling decreases insufficiently (1.5-3.5%), and the degree of purification of the exhaust gas is 70-80% under all operating conditions.

Thus, the reduction in the toxicity of exhaust gases depends not only on the chemical composition of the catalysts, but also on the brand of the engines, and is apparently caused by a different ratio of carbon monoxide to oxygen on the surface of the catalysts depending on the type of engine after an additional suction of air.

The relative concentrations of the reacting components on the catalyst surface may be estimated on the basis of their gas-phase concentration from data obtained by analyzing the exhaust gas for carbon monoxide and oxygen past the gas purifier.

Figure 63 a shows the average oxygen content in the exhaust gases of various engines past the gas purifier under conditions prevailing in Moscow. It is evident that in the composition of the exhaust gas of the "Moskvich-407" engine past the gas purifier, the amount of oxygen ranges from 4 to 8%, which at high initial concentrations of carbon monoxide (4-8%) and hydrogen (up to 3-4%) cannot ensure their complete oxidation, particularly at high space velocities. In the case of other brands of trucks, ZIL-130 (8-12%), GAZ-51 (15-18%), and ZIL-585 (7-11%), the exhaust gas contains a larger amount of oxygen, which ensures a more complete removal of carbon monoxide when the latter is present in the exhaust in more or less appreciable concentrations.

Probably the main reason for a decrease in the efficiency of a catalytic gas purifier at high carbon monoxide concentrations for certain brands of motor vehicles is an insufficient supply of additional air through the injector (the air injection coefficient in all the gas purifiers was the same, about 0.25). At the same time, it is known from the literature that an injector with an adjustable nozzle geometry constitutes the optimum design of a neutralizer injector [76].

This factor had an adverse effect on the degree of removal of carbon monoxide from gasoline engine exhaust in tests under the mountainous conditions of Alma-Ata, where the oxygen content of air is lower. The average oxygen content in the exhaust gas past the gas purifier for all the brands of motor vehicles tested was lower than under Moscow conditions, i. e., did not exceed 3.6-7.0%, and for a PAZ-652 truck, 3.5-5% (Fig. 63 b). The oxidation of higher concentrations of carbon monoxide and hydrogen (the content of hydrogen is as high as 2-6%) requires more substantial oxygen concentrations on the surface of the catalysts than the analysis of the exhaust gas for oxygen past the gas purifier. A consequence of this is a decrease in the degree of removal of carbon monoxide from exhaust gases under the conditions prevailing in Alma-Ata. It should be noted that a decrease in the activity of platinum catalyst (at high carbon monoxide concentrations) is also attributed by a number of foreign researchers to an insufficient amount of air for the oxidation of carbon monoxide.

Table 31.

Catalytic Removal of Carbon Monoxide from Exhaust Gases Under Different Operating Conditions of GAZ-51 Truck in a KN-75 Gas Purifier (Alma-Ata).

Catalyst on aluminosilicate (ΣMe 0.75 wt. %)	Degree of purification of CO, % (maximum values)							
	Idling, rpm		Traveling speed, km/hr					
			No load			Under load.		
	400	1800	30	40	60	30	40	60
Pd	100	55	100	67	69	85	57	23
Pd—Co	74	66	100	75	29	84	31	60
Pd—Cu	97	36	97	44	44	27	0	56
Pd—Pt	51	0	59	22	8	31	16	10

Table 31 presents data (obtained by KazNIPIAT) on the removal of carbon monoxide from the exhaust gases of gasoline engines of GAZ-51 and "Moskvich-408" under road conditions, using different palladium catalysts prepared by the Institute of Chemical Sciences of the Kazakh Academy of Sciences.

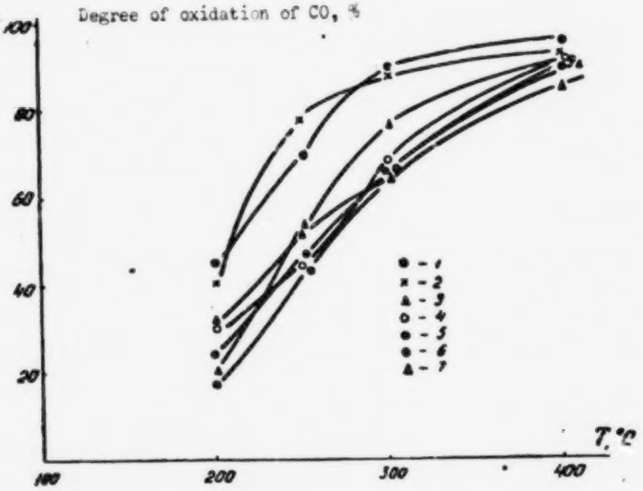

Fig. 64. Change of the activity of palladium catalysts after partial service on GAZ-51 truck in the oxidation reaction of 1% CO in air at 36 x 10^3 hr^{-1} in a laboratory unit: 1 - fresh catalyst; 2-7 - catalysts after service on trucks.

On palladium and palladium-cobalt catalysts, the degree of removal of carbon monoxide from the exhaust gas of the GAZ-51 engine amounts to an average of about 50%; the maximum is 60-100% in idle operation, and drops to 30-60% as the traveling speed increases to 60 km/hr. On palladium-copper and platinum-palladium catalysts, the degree of purification is substantially lower. The same pattern but with a lesser effect is observed in the purification of the exhaust gas of the "Moskvich-408" engine in the KNT-150 gas purifier. In idle running, the degree of oxidation of carbon monoxide is 20-40% on palladium and platinum-palladium catalysts, and during motion under load, it decreases from palladium-cobalt (60-70%) to palladium (20-50%), platinum-palladium (5-30%), and palladium-copper (0-20%) contacts. The averager oxygen content in the exhaust gas past the gas purifier during motion does not exceed 4-5%, i. e., is 2-2.5 times lower than in the exhaust gas of the GAZ-51 engine under conditions prevailing in Moscow (see Fig. 63), and is obviously the main cause of the lessening of the purification effect.

This is confirmed by data on a slight change in the activity of palladium catalysts after partial use, obtained by testing them in a laboratory unit in a stream of air (Fig. 64). The activity of the contacts after one month's use in the GAZ-52 truck decreased by 10-30% at 200-300°C., but remained unchanged at 400°C. The phase composition of the catalysts also remained unchanged.

Table 32.

Phase Composition of Palladium Catalysts.

Intensity	Interplanar spacing d = d/n		Phase
	Found	Tabular data for Pd	
Pd/Sn (0.75 wt. % Pd) after tests on GAZ-52 (Alma-Ata)			
10	2,237	2,246(100)	Palladium
8	1,950	1,945(2)	
9	1,375	1,376(25)	»
10	1,173	1,173(24)	»
7	1,123	1,123(8)	»
Pd/Al_2O_3 (0.5 wt. % Pd) after tests on GAZ-52 (Alma-Ata)			
10	2,237	2,246(100)	Palladium
8	1,950	1,945(42)	
9	1,375	1,376(25)	»
10	1,173	1,173(24)	»
7	1,123	1,123(8)	»
Pd/ShAS (0.75 wt. % Pd) after tests on ZIL-130 (Moscow, 21,000 km on odometer)			
6	4,36	—	—
4	3,87	—	—
5	3,35	—	—
6	3,13	—	—
5	2,76	—	—
7	2,29	2,246(100)	Palladium
4	2,18	—	
10	2,18	—	—
3	2,13	—	—
3	1,966	1,945 (42)	Palladium
2	1,796	—	
3	1,715	—	—
4	1,619	—	—
3	1,492	—	—
1	1,398	—	—
2	1.374	1,376 (25)	Palladium
1	1,348	—	
1	1,220	—	
2	1,172	1,173 (24)	Palladium
2	1,123	1,123 (8)	
1	1,095	—	Palladium
10	1,059	—	
1	1,032	—	—
1	0,995	—	—
1	0,972	—	—
2	0,891	—	—
2	0,869	—	—

Table 33.

Change in the Composition of Exhaust Gases of 50 GAZ-52 Engines during Purification on Pd/ShAS-2 (0.75 wt. % Pd) in KN-175 Gas Purifiers.

Group of vehicles	Gas composition before purifier (range), %			Gas composition past purifier (range), %					
				Samples taken before 500 km on odometer			Samples taken after 500 km on odometer		
	CO	H_2	O_2	CO	H_2	O_2	CO	H_2	O_2
First	0—5,0	0—2,5	4,0—10,0	0—1,0	0—0,5	4,0—10,0	0—4,0	0—1,0	4,0—10,0
Second	0—11,5	2,5—6,0	3,0—11,0	0,0—2,0	0—1,0	3,0—11,0	0—9,0	0—3,0	3,0—11,0

According to x-ray spectra, palladium is in the crystalline state in samples of palladium catalysts on synthetic aluminosilicate after approximately one month's use on GAZ-52 trucks (8 samples, Alma-Ata), on the ZIL-130 truck (one sample, Moscow, 21,000 km on odometer) and also on aluminum oxide (5 samples, GAZ-52, 3-4 thousand km on odometer, Alma-Ata). The interplanar distances on the x-ray patterns of all the samples tested fully corresponded to the interplanar distances of the palladium phase. Thus, in the operation of palladium catalysts in the stream of exhaust gas from GAZ-52 and ZIL-130 engines, the active phase is metallic palladium.

Tests of palladium catalysts on synthetic aluminosilicate carried out in Alma-Ata established that its activity decreases in the course of service.

Table 32 lists data on the content of carbon monoxide, hydrogen, and oxygen in the exhaust gas (for vehicles with 5000 km or more) of 50 GAZ-52 trucks arbitrarily divided into two groups. The first group of trucks consisted of engines whose exhaust composition included over 2.5% hydrogen and carbon monoxide ranging from 0 to 11.0%. The exhaust gases of the second group of trucks (12 out of 50) contained less than 2.5% hydrogen and from 0 to 5% carbon monoxide.

As is evident from Table 33, in the exhaust gas of both the first and second group of trucks, the maximum concentrations of carbon monoxide and hydrogen decreases substantially in the course of catalytic purification when the distance covered is up to 500 km. In a no-load run at 40-60 km/hr, the degree of removal of carbon monoxide varies from 30 to 80%. However, as the catalyst continues to be used on the same vehicles, hydrogen is only half-oxidized, and carbon monoxide is only 20% oxidized. The amount of carbon monoxide in the exhaust gas varies from 1 to 9%, and the degree of purification of most vehicles is 10%, and for some, 30-70%.

When the gas purifiers were taken off the trucks, losses of the catalyst were observed. Figure 65 shows data on the weight decrease of palladium catalysts on synthetic aluminosilicate after partial use on GAZ-52 trucks. The length of service of the truck (in thousand km) is plotted along the horizontal axis, and the catalyst loss (in wt. %) is laid off along the vertical axis.

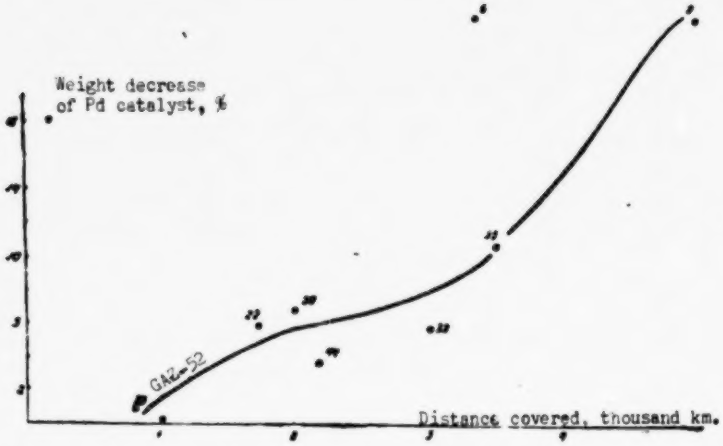

Fig. 65. Decrease in the weight of palladium catalyst on synthetic aluminosilicate in the course of service in a gas purifier on a GAZ-52 truck under conditions prevailing in Alma-Ata.

It is evident that the catalyst losses are particularly significant during the first 2000 km of run (up to 6 wt. %) and increase sharply (up to 10%) during further run, when the catalyst begins to operate with a loose packing in the gas purifier.

In order to evaluate the process of wear of the catalyst granules in the course of service in trucks, the particle size distribution of the catalyst was determined before and after the tests on different vehicles. Results of sifting of catalyst particles from various gas purifiers into fractions are shown in Fig. 66, where the mean diameter of the particles is plotted along the horizontal axis and their weight fraction is plotted along the vertical axis. For comparison, the figure shows the particle size distribution of the initial batch of catalyst poured into the gas purifier.

It is evident from the figure that the particle size distribution of the catalysts changes substantially during service on the trucks. The quantity of particles measuring 4.75-6 mm and 3.75-2.5 mm decreases substantially (to 5 wt. %) in the course of the tests as a result of abrasion into dust. The abrasion of coarse granules forms particles 4.25 mm in diameter whose number increases. However, after the loss of more than 5-6 wt. % of the catalyst, when the latter operates as a moving bed (catalyst from gas purifier 35, Fig. 66), granules larger than 3.5 mm in size break up rapidly; the quantity of particles 4.2 mm in diameter decreases by more than 10%, and a large quantity of fine particles is formed (3.25 mm in diameter or smaller).

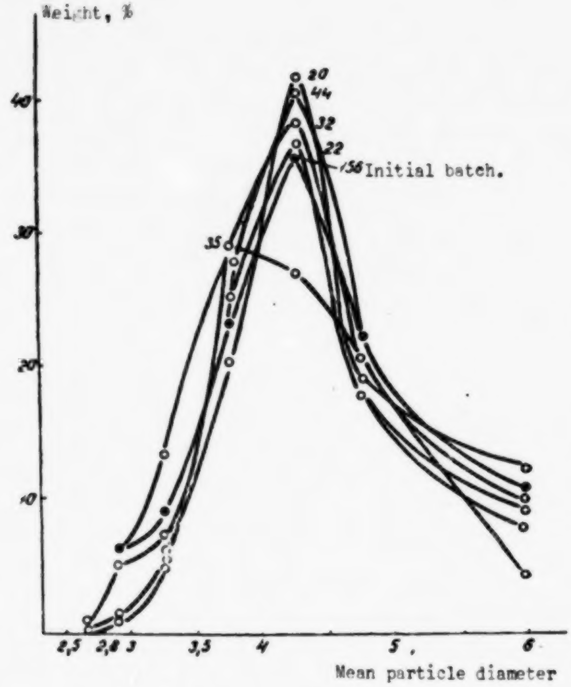

Fig. 66. Change in the fractional composition of palladium catalyst on bead synthetic aluminosilicate in the course of service on GAZ-52 truck.

Analysis of the data obtained after the use of palladium catalyst on synthetic aluminosilicate on trucks shows that the catalyst undergoes mechanical abrasion. Granules of all sizes are abraded to approximately the same extent, but those under-going the greatest abrasion are split or fine granules up to 3 mm in size, which change into dust, the latter being then carried off by the stream of exhaust gas through the catalyst screen. When the weight of the catalyst is reduced by 5-6% on GAZ-52 trucks, the catalyst begins to operate in a moving bed, and the breakdown process accelerates. As a result of breakthrough of the gas into the unoccupied space, the degree of carbon monoxide removal from this gas decreases sharply.

In the development of the technological process of preparation of palladium catalyst on aluminosilicate, particular attention was concentrated on its mechanical strength. The truck tests also included a catalyst whose mechanical abrasion resistance, determined in an eccentric vibratory mill, was 96%. However, the operational strength of the palladium catalyst on synthetic aluminosilicate proved to be inadequate. Apparently, it is determined not so much by the abrasion of particles during jolting, as by the nature of the chemical processes occurring on the surface and by the structure of the catalyst pores. The strength of the catalyst decreases because of exothermic oxidation reactions of hydrogen, carbon monoxide, and hydrocarbons, and the presence of substantial amounts of water vapor in the exhaust gas (up to 5.0%), whose sorption and desorption in the presence of abrupt temperature changes causes cracking and breakdown of a carrier with a connecting porous structure. Slight losses of the catalyst due to cracking (up to 5-6%) create conditions (moving bed) promoting the breakdown of the catalyst, as a result of which channels are formed for the exhaust gas to break through to the side of the main bulk of the catalyst. The fact that the degree of purification is substantially decreased only by the formation of catalyst-free space in the gas purifier is confirmed by data on an insignificant change in the activity of the catalysts after their partial use in motor vehicles under laboratory conditions (see Fig. 64).

Because of the low operational strength of palladium catalyst on synthetic aluminosilicate, its use on trucks is possible only if it is periodically supplemented, which causes an inconvenience in its use. Palladium catalyst on aluminum oxide has a high operational strength and was found more suitable for reliability and durability tests. In tests on various motor vehicles, its efficiency does not decrease in the course of 20,000 km.

Table 34 includes the existing literature data on exhaust purification catalysts which have passed road tests. The bulk of the data were obtained by testing the Houdry platinum catalyst (rods, beads) manufactured by Oxy-France and platinum catalyst on aluminum oxide made in the USSR, tested on gasoline and diesel engines. Platinum catalyst (Oxy-France) was studied in detail by Fitten [31], and in the USSR by NAMI, LANE, and the Karpov Physicochemical Institute [5,44, 64, 67]. For carburetor engines, Fitten notes a high degree of removal of carbon monoxide (50-100%), hydrogen (50-90%), and hydrocarbons (50-90%) under various engine operating conditions (Fig. 67), this removal being determined by the temperature in the catalyst bed: at 500°C. and above, an 80-90% purification is achieved. Fitten points out that the catalyst did not lose its activity (degree of purification above 50%) and did not break down in the course of 17.6 thousand km, but was poisoned by lead compounds present in ethylized fuel.

A platinum oxicat was tested by NAMI and the Institute of Sanitation and Hygiene on stands of "Moskvich-407" and ZIL-164 engines [5]. The degree of removal of carbon monoxide from the exhaust gas was 99.0-99.7%. The domestic platinum catalyst gives a high degree of removal of carbon monoxide (83-100%) for a long period of time.

In the case of exhaust gases of diesel engines [31], the "oxicat" platinum catalyst removes 75% carbon monoxide, 60-85% hydrocarbons, and 60% aldehydes. Similar results were obtained by testing it on the exhaust gas of the YaMZ-236 diesel engine (188 p) at a load of over 50% (60% removal of CO, 100% aldehydes) [64]. A lower degree of removal of CO (46-74%) is obtained over platinum

Table 34

Road Tests of Exhaust Purification Catalysts and Characteristics of Catalytic Gas Purifiers

Catalyst	Type of engine	Operating conditions of engine	Average degree of removal, %, of						Duration of service	Stability to lead and overheating	Country, company, type of gas purifier	Reference
			CO	H_2	Hydrocarbons	Soot	Aldehydes	Nitrogen oxides				
1	2	3	4	5	6	7	8	9	10	11	12	13
Pt/Al_2O_3 on ceramic rods, h = 3 mm, l = 6–8 mm	Carburetor, cylinder volume 2.5–2.75 l, installed on a van with a load-carrying capacity of 4.5 t	All conditions during motion, t = 500–750°C.	50–100	50–90	50–90	—	—	—	17600 km, does not break down	Stable to heat	France, Oxy-France, model V-3	[31]
Pt/Al_2O_3, Oxicat	Diesel	Engine load above 60%	75	—	60–85	—	60	—	—	—	—	[31]
Pt/Al_2O_3, Oxicat	Carburetor	Power 0.5–1 hp, rotational speed of crankshaft 500–2800 rpm, t° after catalyst 350–620°	99–100	—	—	—	—	—	Not tested	Poisoned by lead	France, Oxy-France, V-4	[5]

Table 34 (Continued)

Pt/Al_2O_3, 2-5 mm beads	Four-stroke diesel, YaMZ-236, 180 hp	Load over 50% $t = 300$—600°	60	—	—	—	100	—	Not tested		France, Oxy-France, DN-200, LANE	[64]
V_2O_5, V_2O_5/Al_2O_3	Carburetor	Optimum temperature 500°C.	—	—	60—70	—	—	—	200 hr, 16-18 thousand km, does not break down	Stable to Pb, 200 hr	USA, Ford Motor Co.	[65]
Unknown	Carburetor, diesel	Optimum temperature 420-650°C., start of operation 120°C., idling		Brings the content of CO and hydrocarbons in the exhaust gas down to sanitary norms					32,000 km, abrasion resistant; after 19,000 km no decrease in volume of catalyst was observed	Not poisoned by Pb or S, Overheating to 98°C. allowed	USA, Technical Industries, gas purifier designed by Gulik-Rous	[66]
Unknown	Carburetor	All conditions	80	—	90—95	—	—	—	38,600 km (about two years)	—	USA, Universal Oil Products	[66]
Al, Pt, Cr, Cu	Carburetor, diesel	All conditions	80—95	—	80	—	80	—	1000 hr or 40,000 km for gasoline engine and 3000 hr or 120,000 km for diesel engine	Preheated to 800°C before operation	Japan, Hino Motors Limited	Advertising information

Table 34 (Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
Pd/Al$_2$O$_3$, Spherical ShPAK-0.5	Diesel MAZ-525	Idle revolutions, 25 t load Ascent from and descent into quarry	49—79	—	—	40—50	60—100	—	Not tested	900—1000°	USSR, LANE, UFAN, IKhN ANKaz SSSR, NTK-6M with preheating, fluidized bed	Records of tests
Pd/Al$_2$O$_3$ Spherical	〃	〃	58—79	—	—	25—75	33—91	—	〃	〃	USSR, LANE, UFAN, Karpov Physicochemical Institute, NTK-6M	〃
Oxide catalyst 406-R-4	〃	〃	0—58	—	—	70—100	100	—	〃	—	USSR, LANE, UFAN, Petroleum Chemistry Institute (Baku), NTK-6M	〃
Pt/Al$_2$O$_3$	Gasoline MZMA-407	Load on stand from 25 to 100, 1500-2000 rpm in motion no-load operation, speed 30-70 km/hr at a load of 2.5 t	83—100	—	—	—	—	—	Laboratory-road tests	—	USSR, LANE, KNG-150	〃

Table 32 (Continued)

Pd ShAS-2	"	"	**75—100**	—	—	—	—	—	"	—	USSR, LANE, IKhN ANKaz SSR, KNG-150
Pd/Al_2O_3 spherical ShPAK-0.5	Carburetor engines of ZIL-130, "Moskvich-407", "Volga"	All conditions of motion	**70—100**	—	—	—	—	—	—	—	KN-150
			50 and above,	—	—	—	—	—	—	—	KNG-150
			60 and below	—	—	—	—	—	—	—	KazNIPIAT
	GAZ- 51										
Pd/ShAS-2	Carburetor	"									USSR, LANE, IKhN ANKaz SSR
	GAZ-51		Above 50	—	—	—	—	—	—	—	KN-75
	ZIL-130		**60—100**	—	—	—	—	—	—	—	KN-150
	ZIL-585		50 and above	—	—	—	—	—	—	—	KN-100
	GAZ-51		**20—100**	—	—	—	—	—	-	—	KN-75 KazNIPIAT
Pd/Fe/ ShAS-2	ZIL-130	All conditions									USSR, LANE, IKhN ANKaz SSR, KN-150
		No-load operation, 30 km/hr,	**70—100**								
		50-60 km/hr	**45—65**	—	—	—	—	—	—	—	Moscow
Pd/Co ShAS-2	GAZ-51	All conditions	60 and below	—	—	—	—	—	—	—	USSR, IKhN AN KazSSR, KazNIPIAT, KN-75, Alma-Ata

(bead) catalyst on aluminum oxide in KNG-250 and KNG-300 gas purifiers [67] in the operation of carburetor and diesel motor vehicles at a traveling speed of 15-20 km/hr. In the exhaust gas of carburetor engines, carbon monoxide decreased by 46-54%, and nitrogen oxides by 50-56%, and in the case of diesel engines, carbon monoxide by 58-74% and nitrogen oxides by 30-56%.

Contamination of catalysts with fuel residues and soot (at moderate temperatures) curtail the service life of the contact: instead of 2500 hours, it is shortened to 1200-1400 hours (diesel) and 1600 hours (carburetor engine). For this reason, a composite gas purifier designed by LANE and a thermocatalytic purifier designed by Filatov, which have been road-tested, are obviously more suitable for the purification of diesel engine exhausts under all conditions.

In addition to palladium catalysts, of great interest is a catalyst consisting of aluminum, platinum, chromium, and copper, proposed by the Japanese company Himo Motors Linited for the purification of exhaust gases of gasoline and diesel engines. According to the description, it removes 80-95% of carbon monoxide, 60% of the hydrocarbons and 80% of the aldehydes from the exhaust, and is stable for 40,000 km for gasoline engines and 120,000 km for Diesel engines. A vanadium catalyst on aluminum oxide and without a carrier, proposed by Ford Motor Co., was found to be stable to poisoning with lead compounds [65] for 200 hours of operation. In its presence, the oxidation of hydrocarbons (60-70%) and particularly olefins and paraffins (50-90% at 250°C.) is satisfactory, and carbon monoxide is oxidized starting at 500°C. only at low space velocities.

For carburetor engines, certain US firms [66] propose gas purifiers with catalysts (whose composition is unknown to us) which provide a high degree of removal of carbon monoxide (up to 80%) and hydrocarbons (90-95%) from the exhaust; they are stable in operation (up to 38,000 km) and are not poisoned by lead. However, this information cannot be discussed without published reports.

Analysis of the road tests shows that palladium catalyst on bead aluminum oxide is the most efficient catalyst and most promising economically for the removal of carbon monoxide from gasoline engine exhausts.

In the purification of diesel engine exhausts, in which the bulk of the toxic components consists of aldehydes, hydrocarbons and nitrogen oxides, the most promising is the use of platinum, palladium with preheating of the gas (combined or thermocatalytic gas purifiers) and particularly oxide catalysts and natural activated manganese, copper and iron ores, which ensure the oxidation of the toxic components at a low temperature and are characterized by a low cost.

The use of the method of catalytic purification of exhaust gases of motor vehicles operating on ethyl gasoline will require further studies aimed at selecting catalysts which are not poisoned by lead compounds. Apparently, a composite gas purifier is needed for all the gases, in the first compartment of which nitrogen oxides will be removed from the exhaust gases without injection of extra air and in the second compartment (in an oxidizing medium), carbon monoxide and other organic compounds (aldehydes, hydrocarbons) will be removed. In each compartment of the composite gas purifier, the optimum catalyst for the removal of the respective components will probably be installed.

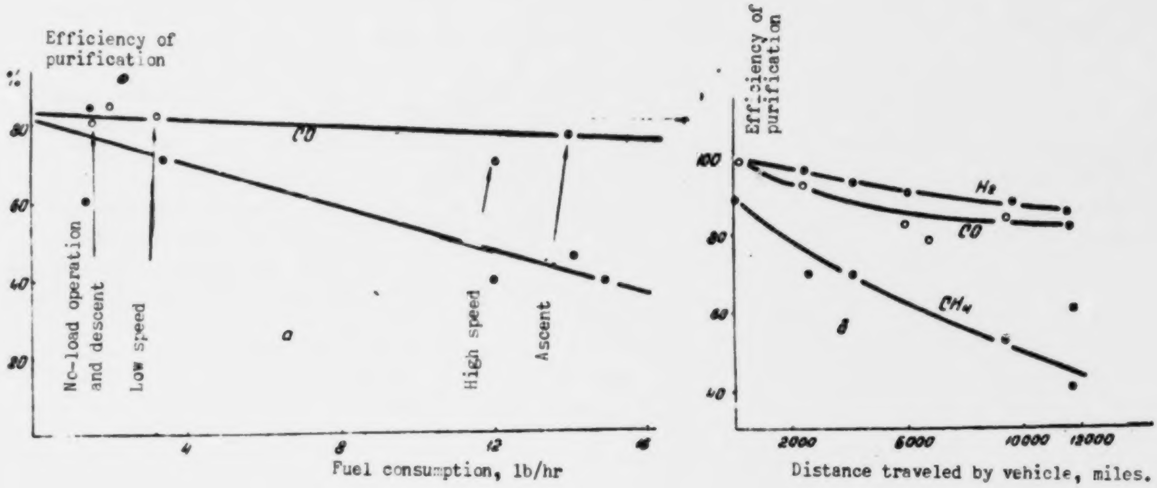

Fig. 67. Efficiency of platinum catalyst in the purification of the exhaust gas of a carburetor engine in Fitten's experiments (cited in [5]): a - during changing operating conditions of engine; b - as the distance traveled by the vehicle increases.

LITERATURE CITED

1. Байков Б. К., Фельдман Ю. Г. — «Гигиена и санитария», 1966, № 12, 3.

2. Шестерикова К. П., Строгальщикова П. Н. — «Гигиена и санитария», 1965, № 5, 73.

3. Девятка В. Г. — «Гигиена и санитария», 1960, № 1, 90.

4. Вольфсон З. Г. — В сб.: «Предельно допустимые концентрации атмосферных загрязнений», вып. 1. М., Медгиз, 1952.

5. Коренев М. С. Пути уменьшения вредности отработанных газов автомобильных двигателей, серия XII, Автомобилестроение. М., ЦИНТИМаш, 1962.

6. Гершенович М. С., Котелков Н. З. — «Мотор», 1938, № 4 31—33.

7. Великанов Д. Д., Ставров Д. А. — «Изв. АН СССР, энергетика и транспорт», 1960, 3, 143—149.

8. Бердыев Х. Б., Павлович Н. В., Тужилина А. А. — «Гигиена и санитария», 1967, № 6, 96.

9. Неменко В. А. Загрязнение атмосферного воздуха 3,4-бензпиреном в некоторых городах Казахстана. Автореферат диссертации. Алма-Ата, 1967; Неменко В. А. — Труды Каз. научно-исследоват. ин-та онкологии и радиологии, 1967, 3, 46.

10. Heimann Harry. Загрязнение атмосферного воздуха. Женева. Всемирная организация здравоохранения, 1961, 171.

11. Кочнев К., Васильев М., Филатов С. — «Автомобильный транспорт», 1962, № 1, 19.

12. Филатов С. С. — Труды горно-геологического института, вып. 55. Свердловск, 1960, 85.

13. Кущенский К. С., Росемит А. Ф. — «Бюллетень Центр. научно-исследоват. института информации и тех.-эконом. исследований черной металлургии», 1964, № 18, 494.

14. Варшавский И. Л. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 5.

15. Петрова Д., Далакманский Ю., Битколов Д. — «Ж. гигиены, эпидемиологии, микробиологии и иммунологии», 1966, 10, № 3, 357.

16. Девятка В. Г. — «Врачебное дело», 1955, № 4, 341.

17. Битколов Н. З. Нейтрализация выхлопных газов и вентиляция при работе дизельного оборудования в подземных условиях. М., УПИИ физико-экон. исследовательской металлургии, 1965.

18. Бадский Е. Б. Физиология человека. М., «Медицина, 1966.

19. Лазарев Н. В. Руководство по фармакологии, 1. М., Медгиз, 1964.

20. Битколов Н. З. Очистка выхлопных газов двигателей внутреннего сгорания. М., 1962.

21. Almgnist J. A., Bray W. C. — «J. Amer. chem. Soc.», 1923, 45, 2305.

22. Лазарев Н. В. Вредные вещества в промышленности. Л., Госхимиздат, 1963, стр. 290.

23. Martin H. — «Automobiltechn. Z.», 1965, 4, 113.

24. Петер Б., Шмидт П. — «Гигиена и санитария», 1966, № 7, 91.

25. Парцеф Д. П. — «Гигиена и санитария», 1966, № 9, 11—14.

26. Мачульский Ф. Ф. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 206.

27. Шабад Л. М., Хесина А. Я. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 57.

28. Самойлович Л. Н., Редькин Ю. Р. — «Гигиена и санитария», 1968, № 9, 14.

29. Чуриков Б. П., Шабад Л. М. и др. — «Гигиена и санитария», 1962, № 2, 19.

30. Шабад Л. М., Дикун П. П. Загрязнение атмосферного воздуха канцерогенным веществом. М., Медгиз, 1959, стр. 138, 163, 186.

31. Fitten A. Internat. Automobil. Techn. Congress, 8-th, Harlem. Proceeding, 1960, 174 p.

32. Бейлк К. Л., Джейбс А. Р., Локк Д. К. — В сб.: «V Международный нефтяной конгресс. Транспорт, качество, применение нефтепродуктов». М., Гостоптехиздат, 1961, стр. 204.

33. Glover J. — «J. Inst. Petrol.», 1966, 52, № 509, 137, 154.

34. «Engineering», 1967, 203, № 5260, 213.

35. Lönner K., Müller H., Lander W. — «Motortechn. Z.», 27, № 7, 1966, 271.

36. Алексеева М. В., Озерский А. С., Хрусталева В. А. — «Гигиена и санитария», 1962, № 12, 3.

37. Славолюбов С. С. — «Изв. высш. учеб. заведений, серия машиностроение», 1966, № 2, 92.

38. Варшавский И. Л., Золотаревский Л. С., Игнатович Л. Е. — «Автомоб. пром-сть», 1967, 33, № 6. В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, 33.

39. Манусаджянц Ж. Г., Степанов Л. Л. — «Городское хозяйство Москвы», 1965, № 12, 13.

40. Doniselly C. «La corresione borometrica der rapporto combustibilo aria nei motori otto ad incezione», ATA, 1965, 1, 15—26.

41. Григорьян В. Т., Гаргала Р. В., Малов Р. В. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 365.

42. Загрязнение атмосферного воздуха. Всемирная организация здравоохранения. Женева, 1962, № 46, стр. 187.

43. Raymond Leopard — «S. A. E. Journal», 1964, 72, № 8, 48.

44. Деревянкин М. Е. — «Городское хозяйство Москвы», 1965, № 12, 9.

45. Варшавский И. Л., Золотаревский Л. С., Френкель А. И.— «Газовая промышленность», 1966, № 7, 36.

46. Гуссак Л. Я. — «Природа», 1964, № 3, 86.

47. Вольфсон З. Г. — «Гигиена и санитария», 1948, № 1, 73.

48. Соколовский М. С., Чабинов Ж. Л., Попов Б. В., Качар Л. Ф. Санитарная охрана атмосферного воздуха Москвы. М., «Медицина», 1965.

49. Schalter M. J. — Экспресс-информация. «Автомобильный транспорт», 1968, № 2, стр. 28.

50. Закумбаева Г. Д., Носкова Н. Ф., Конаев Э. Н., Сокольский Д. В. — Автор. свид. СССР № 191487, 31.1.1964.

51. Закумбаева Г. Д., Носкова Н. Ф., Конаев Э. Н., Сокольский Д. В. — Автор. свид. СССР № 177021, 16. 11. 1963.

52. Недогибченко М. К. — «Гигиена и санитария», 1958, № 8, 6.

53. Яскулла Н., Веттиг К., Риттер Э. — «Гигиена и санитария», 1967, № 8, 86.

54. Сокольский Д. В., Попова Н. М., Сыздыкбаева М. Б. — Труды Ин-та хим. наук АН КазССР, т. 13. Алма-Ата, 1965, стр. 70.

55. Чалабов В. Г. Исследование влияния некоторых эксплуатационных факторов на состав отработанных газов автомобильных двига-

телей и выбор методов снижения их токсичности. Автореферат диссертации. М., 1968.

56. Сыздыкбаева М. Б., Попова Н. М., Сокольский Д. В. — «Изв. АН КазССР, сер. хим.», 1967, вып. 4, 37.

57. Сокольский Д. В., Попова Н. М., Сыздыкбаева М. Б., Муканова Б. С., Самсонова Н. С. — «Изв. АН КазССР, сер. хим.», 1966, вып. 2, 42.

58. Сокольский Д. В., Попова Н. М., Закумбаева Г. Д., Носкова Н. Ф., Алексеева Г. К., Сыздыкбаева М. Б. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 63.

59. Сокольский Д. В., Попова Н. М., Закумбаева Г. Д., Носкова Н. Ф., Алексеева Г. К., Сыздыкбаева М. Б., Шуматева Н. Ф.— В сб.: «Развитие производительных сил Южного Казахстана». Алма-Ата, «Наука», 1966, 3, стр. 138.

60. Сокольский Д. В., Попова Н. М., Закумбаева Г. Д., Носкова Н. Ф., Алексеева Г. К., Сыздыкбаева М. Б., Шуматева Н. Ф. — Тезисы конференции по развитию производительных сил Южного Казахстана. Алма-Ата, «Наука», 1964, стр. 192.

61. Сокольский Д. В., Попова Н. М. и др. — Труды ин-та хим. наук АН КазССР, 1968, 22, стр. 3.

62. Сокольский Д. В., Друзь В. А. и др. — Труды Ин-та хим. наук АН КазССР, 1965, 13, 75—201.

63. Филатов С. С., Кочнев К. В., Васильев М. В. — «Горный журнал», 1960, № 5, стр. 65.

64. Малов Р. В., Гаргала Р. В.— «Горный журнал», 1964, № 8, 73.

65. SAE Journal, 66, 1958, № 1, 36. (Перевод ЦБТИ Мосгорсовнархоза).

66. Faith W. Z., Renuzetti N. A. — Seventh techn. progress report, 1966, II p.

67. Краснокутский Н. П.— «Горный журнал», 1968, № 2, 66.

68. Ивановский Ф. П., Семенова Т. А., Маркина М. И., Штейнберг Б. И., Будкина О. Г., Хитрова Н. Ф., Ващинина А. Е.— Химия и технология минеральных удобрений. Очистка газа. Отдел научно-техн. информ. М., 1965, стр. 5.

69. Поповиченко Р. М., Ромашкин М. И. — «Вестн. АН КазССР, 1960, № 12, 10.

70. Гончаров В. В., Малов Р. В. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 172.

72. Беленький М. З., Султанов М. Ю. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 105.

72. Филатов С. С. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 313.

73. Малов Р. В. — В сб.: «Токсичность двигателей внутреннего сгорания». М., «Наука», 1966, стр. 137.

74. Комаров Н. И. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 189.

75. Закумбаева Г. Д., Носкова Н. Ф., Сокольский Д. В., Конаев Э. Н — «Докл. АН СССР», 1964, 159, № 6, 820.

76. Дорин В. А. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., «Наука», 1966, стр. 155.

77. Алексеевский Е. В. — «Ж. прикл. химии», 1929, 2, № 6, 780.

78. Предельно допустимые концентрации атмосферных загрязнений, вып. 8. М., Медгиз, 1964, стр. 190.

79. Горфункель В. Е. — В кн.: «Очистка и использование сточных вод и промышленных выбросов». Киев, Ин-т техн. информации, 1964, стр. 93.

80. Тихоненко А. Д., Набиев М. Н. — «Узб. хим. журнал», 1967, № 4, 6.

81. Кулик А. А., Тихоненко А. Д. — «Вестн. техн. и экон. информации». М., НИИТЭХИМ, 1962, № 5, стр. 57.

82. Houdry E., Harrison J. W. Производство механически прочного катализатора. Пат. США № 2889288, 2. 6. 1959.

83. Houdry E. — «Катализ». Труды первого международного конгресса. М., ИЛ, 1960, 562.

84. Алексеевский Е. В., Макаров И. Д. — «Ж. прикл. химии», 1930, 3, № 6, 853.

85. Алексеева Г. Н., Ризов З. М., Тодес О. М. — «Кинетика и катализ», 1961, 2, вып. 3, 400.

86. Захаров Б. А., Николаева Т. Н. — «Изв. АН СССР, ОТН», 1948, № 1, 79.

87. Connon W. A., Welling C. E. — «Ind. Eng. Chem.», 1962, 1, № 3, 152.

88. Gunther Arnold. — Пат. США, kl. 252—474, № 3206414, 14. 09. 65, приоритет 10. 7. 62.

89. Sourirayan S. — «Canad. J. Chem. Engng.», 1961, 39, № 2, 68.

90. Султанов М. Ю., Беленький М. С. — «Изв. вузов. Нефть и газ», 1962, № 9, 57.

91. Ахундова М. Р., Беленький М. С. — «Нефть и газ», 1960, № 12, 73.

92. Ройтер В. А., Рубаник М. Я., Снигуровская Ю. А., Садовникова Е. А. — «Ж. прикл. химии», 1945, 18, № 7—8, 450.

93. Ройтер В. А., Туровский Г. Я. — «Кислород», 1957, № 5, 14.

94. Ройтер В. А. — «Ж. физ. химии», 1940, 14, № 9—10, 1370.

95. Вендт В. П., Лебедева Т. А. — «Зав. лаб.», 1958, 7, 818.

96. Johnson E., Christian G., Carhart H. W. — «Ind. and Engng. Chem.», 1961, 53, № 11, 900.

97. Марголис Л. Я., Тодес О. М. — «Изв. АН СССР, ОХН», 1947, № 5, 443; 1946, 52, № 6, 519.

98. Christian J. C., Johnson J. E. — «Air and Water Pollution», 1965, 9, № 12, 1.

99. Фастовский В. Г., Мамосов В. А. — «Ж. прикл. химии», 1940, 8, № 12, 1839.

100. Ruff R. I — «Heat and Ventilation», 1953, 50, № 9, 84; «Chem. Eng. Progress», 1957, 53, № 8, 377.

101. «Ind. Gas.», 1953, 31, № 8—9, 24.

102. Vallheim Ceerhard — «Staub», 1965, 25, № 11, 466.

103. Кравченко В. С., Биренберг И. Э., Волков В. В., Карпов Е. Ф., Магидсон И. А. Способ получения катализатора для сжигания метана в газоанализаторах. Авт. свид. СССР, 118495, 1958.

104. Cabe C. Mc. — «Ind. Eng. Chem.», 45, 1953, № 4, 115A; — «Safety Maintinance and Production», 106, 1953, № 3, 53; Steel, 1955, 136, № 4, 84.

105. Аманазевич Е. И. и др. — Труды Куйбыш. н.-иссл. ин-та нефт. пром., 1964, вып. 25, 197.

106. Cohn J. G. E. Метод окисления газов, содержащих метан и кислород. Пат. США, kl. 23—2. 3056646.

107. Gunther Arnold. — Пат. США 2983372, заявлено 9.08.62 опубликовано 17. 02. 65.

108. Schnetze M., Buschamann, Ermshans H. D. — Бельг. пат. COIB, 620912, заявлено 31.07.62, опубликовано 31.01.63.

109. Миначев Х. М., Кондратьев Д. А., Антошин Г. В. — «Кинетика и катализ», 1967, 8, вып. 1, 131.

110. Sourirayan S., Accomazzo M. A.— «Canad. J. Chem.», 1960, 38, № 10, 1900.

111. Accomazzo M. A., Nobe K. — «Ind. Eng. Chem. Process Design Developm». 1965, 4, № 4, 425.

112. Stein K. C., Feenan J. J., Thompson G. P., Schultz J. F., Hofer L. J. E., Anderson R. B. — «Ind. Eng. Chem.», 1960, 52, № 8, 671.

113. Алексеева Г. К., Сокольский Д. В. — Труды Ин-та хим. наук АН КазССР, 1968, 22, стр. 13.

114. Алексеева Г. К., Сокольский Д. В., Лабода А. И., Михайлов В. А., Котова Г. Н. — Труды Ин-та хим. наук АН КазССР, 1968, 22, стр. 23.

115. Филатов С. С.— В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 313.

116. Гарпушина А. С. — Авт. св-во СССР, 176804 28.12.1965.

117. Naybar M., Ruchynka K., Klier K.— «Collect. Czechoslov. Chem. Com». 1966, 31, № 3, p. 956.

118. Ильченко Н. И., Юза В. А. — В сб.: «Катализ и катализаторы». Киев, 1966, 2.

119. Ильченко Н. И. Исследование влияния небольших добавок платины на каталитическую активность V_2O_5 в отношении окисления H_2 и на кинетику восстановления окислов ванадия». Автореферат диссертации. Киев, 1967.

120. Katz M., Halpern S. — «Ind. and Eng. Chem.», 1950, 42, № 2, 345.

121. Fiedler Bohuslav, Jozef Draharad, Dusan Picha — Пат. Чехословакии, 91318, 61в; 1/02; 15.08.59.

122. Rease R. N. — Пат. США 2838462, kl. 252—471, 10.06.58.

123. Briggs W. E. Очистка выхлопных газов. Пат. США 3288558, kl 23—2, 29.11.1966.

124. Stephens Ruth E., Hirschler Daniel A. — Пат. США, kl. 252—460, № 3324981 оп. 21.12.65.

125. Bloch Herrmann — Пат. США, kl. 23—2, № 3072457, 8.01.63.

126. Edward Michalko — Пат. США, kl 252—413, 3112277, 19.9.1960.

127. Равич М. Б., Захаров В. А. — «Докл. АН СССР», 1940, 26, № 1, 64.

128. Беленький М. С., Алхазов Т. Г., Мальян А. Н. — «Изв. вузов. Нефть и газ», 1960, № 10, 83.

129. Алхазов Т. Г., Беленький М. С. — «Изв. вузов. Нефть и газ», 1959, № 6, 59.

130. Алхазов Т. Г., Беленький М. С. — «Изв. вузов. Нефть и газ», 1959, № 11, 83.

131. Султанов М. Ю., Беленький М. С. — «Изв. вузов. Нефть и газ», 1963, № 2, 50.

132. Полак В. Е. — «Гигиена и санитария», 1968, № 5, 107.

133. Economy J., Mellon D. M., Ostrozynski R. L. — «J. Catalysis», 1965, 4, № 4, 446.

134. Herrmann E. — «Chem. Ind. Techn.», 1965, № 9, 37, 905.

135. Rienäcker G. — «Z. anorg. allgem. chem.», 1949, 238, 280; Rienäcker G. — «Birkenstead., Z. anorg. chem.», 1959, 262, 81.

136. Foulon A. — «Plastverarbeiter», 1965, 16, № 4, 24.

137. Betz E. C., Feist H. J. — «Ind. — Anz.» 1964, 86, № 100.

138. Марголис Л. Я. Тодес О. М. — «Ж. общ. хим.», 1950, 20, 1981.

139. Марголис Л. Я. — «Усп. хим.», 1951, 20, 176.

140. Марголис Л. Я., Крылов О. В. — «Ж. общ. хим.», 1950, 20, 1991.

141. Захаров Б. А., Дурынина Л. И. — «Докл. АН СССР», 1948, 63, № 3, 289.

142. Anderson R. B., Stein K. C., Feenan J. J., Hofer L. J. E.— «Ind. Eng. Chem.». 1961, 53, 809, № 10.

143. Bransom S., Haulon L., Smythe B. — «Trans. Farad. Soc.», 1956, 52, № 5, 672.

144. Blumenthal L., Nobe K. — «Ind. Eng. Chem. Progress Design. Developm.», 1966, 5, № 2, 117.

145. Caretto L. S., Nobe K. — «Ind. Eng. Chem. Progress Design. Developm.», 1966, 5, № 3, 217.

146. Марголис Л. Я., Тодес О. М.— «Ж. общ. хим.», 1948, 18, вып. 6, 1043.

147. Андрушкевич Т. В., Поповский В. В., Боресков Г. К. — «Кинетика и катализ», 1965, 6, № 5, 860.

148. Туровский Г. Л., Саинцова Л. Г., Судак А. Ф., Набиванец Е. И. — «Катализ и катализаторы», Киев, «Наука», 1967, 3, стр. 88.

149. Алексеевский Е. В., Фрид К. В. — «Ж. общ. хим.», 1945, 15, стр. 3.

150. Линде В. Р., Марголис Л. Я., Рогинский С. З. — «Докл. АН СССР», 1961, 136, № 4, 360.

151. Боресков Г. К., Дзисяк А. П., Касаткина Л. А. — «Кинетика и катализ», 1963, 4, № 3, 388.

152. Schachner Herbert. — «Rev Assop. pevent Pollut. atmosph.», 1961, 3, 265, стр. 1.

153. Варшавский И. Л., Малов Р. М. Как обезвредить отработавшие газы автомобиля. М., «Транспорт», 1968.

154. Dmuchovsky L. F. — «J. Catalysis», 1965, 4, № 5, 174.

155. Рубаник М. Я., Холявенко К. М., Гершингорина А. В., Лазукин В. И. — «Кинетика и катализ», 1964, 5, № 4, 666.

156. Hoot W. F., Kobe K. A. — «Ind. Eng. Chem.» 1955, 47, 776.

157. Беленький М. С., Султанов М. Ю. — В сб.: «Токсичность двигателей внутреннего сгорания и пути ее снижения». М., 1966, стр. 105.

158. Алхазов Т. Г., Беленький М. С. — «Изв. вузов, Нефть и газ», 1960, № 8, 87; 1960 № 3, 73.

159. Cohen A. E., Nobe K. — «Ind. Eng. Chem. Progress Design. Developm.», 1966, 5, № 3, 214.

160. Ильченко Н. И., Юза В. А., Ройтер В. А. — «Докл. АН СССР», 1967, 172, № 1, 133.

161. Боресков Г. К., Поповский В. В., Сазонов В. А. — 4 Международный конгресс по катализу. М., 1968, 33 доклад.

162. Кац М. — В сб.: «Катализаторы органических реакций». М., ИЛ., 1955, стр. 291.

163. Голодец Г. И. — «Катализ и катализаторы», 1966, т. 2., стр. 25.

164. Марголис Л. Я. — «Успехи химии», 1959, 28, вып. 5, стр. 615.

165. Lamb A., Bray W. C., Frazer J. C. W. — «Ind Fng. Chem.», 1920, 12, 213.

166. Whiteselel W. A., Frazer J. C. W. — «J. Am. Chem. Soc.», 1923, 45, 2811.

167. Frazer J. C. W., Greider C. E. — «J. Phys. Chem», 1925, 24, 1099.

168. Frazer J. C. W. — «J. Phys. Chem.», 1931, 35, 405.

169. Алексеевский Е. В., Гольбрайх З. Е., Рачинский Ф. Ю., Соскинд А. С., Томилов В. И. Активная двуокись марганца. Л., Химтеоретиздат, 1937.

170. Марголис Л. Я. Каталитическое окисление углеводородов. Л.,«Химия», 1967.

171. Аланова Т. Г., Марголис Л. Я. — Тезисы докл. конференции по методам очистки газовых выбросов и пром. стоков от вредных веществ. Дзержинск, 1967, стр. 228: Хим. пром-сть, 1968, № 1, 30.

172. Казаматкин Е. П., Салтанов В. С., Лобашов К. А. — Тезисы докл. конференции по методам очистки газовых выбросов и пром. стоков от вредных веществ, Дзержинск, 1967.

173. Лобашов К. А. и др. — ЖВХО им. Д. И. Менделеева, 1961, 6, № 2, 173.

174. Rienäcker G. — Abhandl. Dtsch. Akad. Wiss. Berlin kl. «Chem. Geol., Biol.», 1955, № 3, 47.

175. Дроздов Н. П., Малев В. П. — Тезисы докладов конференции по методам очистки газовых выбросов и пром. стоков от вредных веществ. Дзержинск, 1967.

176. Stiles Alvin B. — Пат. США, kl. 23—2, № 3230034 от 18.01.66.

177. E. J. Du Pont de Nemours and Co. Катализаторы дожигания выхлопных газов. Франц. пат. 1397471, 22.03.65, BOI, C1OI.

178. Stiles Alvin B. — Пат. США 3230182, 18.01.66, kl. 252—465.

179. American. Cyanamid company. Состав катализатора для окисления примесей в газах. Франц. пат. 1289490, 8.3 1961, BO1I.

180. Société Francaise de Produits pour catalyse «Procatalyse». Катализатор дожигания выхлопных газов. Франц. пат. 1407059, 21.06.65, BO1I, C1OI.

181. Barrett W. F., Triggiani L. V., Magee J. S. Способ очистки выхлопных газов. Пат. США 3322491, 30.5.1967, kl. 23—2.

182. Cohn J. G. E., Haley A. J. Полное окисление метана. Canad. Pat. 597459, 3.5.1960.

183. Kearby K. K. Способ очистки выхлопных газов. Пат. США 3291564, 13.10.1966, kl. 23—2.

184. Stephens Ruht E. — Пат. США 3224831, 21.12.1965, kl. 23—2.

185. Rucke Douglas, August Charles, Engter Friedrich, Koberstein Engar. — Англ. пат. 1034621, 29.06.1966, B1F, F1B.

186. Сазонов В. А., Поповский В. В., Боресков Г. К. — «Кинетика и катализ», 1968, 9, вып. 2, 312.

187. Adams C. H., Benesi H. A., Curtis R. M., Meisenneimer R. C. — «J. Catalysis», 1962, № 4, 336.

188. Грязнов В. М., Симанов Ю. П., Усова Л. К., Фрост А. В. — «Вестник Моск. гос. ун-та, сер. хим.», 1949, № 5, 79.

189. Грязнов В. М., Усова Л. К., Фрост А. В. — «Вестник Моск. ун-та, сер. хим.», 1949, № 3, 107.

190. Чесалова В. С., Боресков Г. К. — «Докл. АН СССР», 1952, 85, № 2, 377.

191. Алчуджан А. А., Мантикян М. А. — «Ж. физ. хим.», 1959, 33, вып. 4, 780.

192. Миначев Х. М., Ходаков Ю. С. — «Изв. АН СССР, отд. хим. наук», 1961, № 4, 722.

193. Миначев Х. М., Шуйкин Н. И., Феофанов Л. М., Егоров Ю. П. — «Изв. АН СССР, отд. хим. наук», 1957, № 10, 1218.

194. Боресков Г. К., Карнаухов А. П. — «Ж. физ. хим.», 1952, 26, вып. 12, 1814.

195. Миначев Х. М., Гаранин В. И. — «Изв. АН СССР, отд. хим. наук», 1963, № 3, 528.

196. Воронин В. С., Никулина В. С., Полторак О. М. — «Вестник Моск. гос. ун-та, серия хим.», 1963, № 3, 24.

197. Щербаев А. Н., Фурман Н. И., Сотниченко Б. Ф., Самойленко С. М., Денисенко С. А., Эренбург И. И., Марченко А. А., Онопа Б. Н., Тельная Н. В. Способ приготовления измерит. термокатализатора метана. Авт. св-во СССР, 207881, 1.03.68. kl. 12g.

198. Oxy-Catalyst Inc. Способ приготовления катализатора. Франц. пат. Kl Boij, c. 10, № 1360494, 31.03.64.

199. Бурсиан Н. Р., Коган С. Б., Давыдова З. А. Способ приготовления палладиевого катализатора для ароматизации парафиновых углеводородов. Авт. св-во СССР; 176256 от 0 4.11 1963.

200. Rosenblatt E. F., Orange E. N. J. Процесс приготовления нанесенного катализатора платиновой группы. Пат. США, kl. 252—460, № 2475155, 27.12.1945.

201. Cleaver D. H. Производство катализатора группы платины. Пат. США 2982741, kl. 252—466, 2.V 1961.

202. Likins M., Strotman F. и др. Селективное гидрирование и палладиевый катализатор. Пат. США 2946829, kl. 260—677, 26.07.60.

203. Долгов Б. Н. Катализ в органической химии. Л., Госхимиздат, 1959, стр. 187.

204. Beck John Hubert, Stiles Alvin Barber. Получение катализаторов на носителях. Пат. США № 3161605, 252—455, 15.12.64.

205. Koch J. H. Катализаторы, содержащие рутений, и методы увеличения их активности. Пат. США 3055840, kl. 252—443, 25.9.1962.

206. Lacev R. N. Катализаторы на носителях. Англ. пат., № 814003, сентябрь, 1959.

207. Миначев Х. М., Шуйкин Н. И., Марков М. А. — «Изв. АН СССР, отд. хим. наук», 1960, № 5, 907.

208. Natta G., Rigamonti R. Nandbuch der Katalyse, 5, Heterogene Katalyse II, Wien. Spinger — Verlag, 1957, 660.

209. Smith M. A. Изготовление алюминиево-платиновых катализаторов. Пат. США № 2826655, 24.XI 1953.

210. Smith Robert M. Получение платинового катализатора на окиси алюминия. Пат. США, № 3003973, 10.10.61.

211. Алексеевский Е. В., Мусакин А. П., Макаров И. Д. — «Ж. прикл. хим.», 1930, 3, № 6, 863.

212. Алексеевский Е. В., Макаров И. Д. — «Ж. прикл. хим.», 1930, 3, № 6, 857.

213. Алексеевский Е. В. Способ приготовления палладиевого катализатора. Авт. св.-во СССР, 24 389, декабрь, 1931.

214. Sprauer I. W., Falls N. J. Приготовление катализаторов платиновой группы. Пат. США № 2802794, kl. 252—466, 13.VIII 1957.

215. Либерман А. Л., Шнабель К. Х., Васина Т. В., Казанский Б. А. — «Кинетика и катализ», 1961, 2, вып. 3, 446.

216. Новые катализаторы на основе металла семейства платины, их получение и применение. Франц. пат. BOI № 1400636, 20. 04. 65.

217. Kucke Dauglas, August Charles и др. Улучшение катализаторов очистки выхлопных газов. Англ. пат. BIE (BOII), № 1031775, 2.06.66.

218. Алексеев Г. Н., Ризов З. М., Тодес О. М. — «Кинетика и катализ», 1961, 2, вып. 3, 400.

219. Гахахаси Харуо, Морисита Ясусада, Сибата Гоеда. Нанесение металлических покрытий химическим восстановлением. Япон. пат. № 11206, 12А, 211, 16.08.62, РЖХим 1965, 23 Л 284.

220. Ветцель Клаус. Способ получения металлических катализаторов гидрирования. Авт. св-во СССР, 168648, 12 g, 11.03.65.

221. Klarby Kenneth. Получение платинового катализатора на молекулярном сите. Пат. США № 3177152, kl. 252—455, 6.04.65.

222. Coll Edward L., Knowles Edwin C. Катализатор на носителе. Пат. США № 3155627, kl. 252—477, 3.11.64.

223. Полковников Б. Д., Хидекель М. Л., Дмитриева Н. Ф., Микос Э. П., Варушенко В. М. — «Докл. АН СССР», 1968, 181, № 1, 125.

224. Schwarzenbeck E. T., Kellogg M. W. Катализаторы конверсии углеводородов и других процессов. Пат. США № 2989489, kl. 252—466, 27.12.1954.

225. Edward Michalko, Holkstra J., Park E., Smith R. M. Метод получения катализатора. Пат. США № 2927088, kl. 252—466, ноябрь 1956.

226. Casch W., Semeniuk K., Harting W. — «J. Org. Chem.», 1956, 21, № 9, 999.

227. Адаменкова М. Д. Полторак О. М. — «Вестник Моск. гос. ун-та, сер. хим.», 1963, № 5, 12.

228. Connor D., Shipley K. Катализаторы, содержащие платину, и метод их изготовления. Пат. США № 2884374, 22.10. 1954.

229. Mignel Jeen. Катализатор конверсии углеводородов. Франц. пат. № 1331356, kl. BO1I, CIOg, 27.05.63.

230. Буховец С. В. Способ получения платинового катализатора. Авт. св-во № 105486, kl. BOIJ, 12g, 4 01, COIg, 12n, 18.XII 65.

231. Буховец С. В. Способ получения палладиевого катализатора. Авт. св-во № 166307, 12g, 4/01, 18.XI 1964.

232. Сокольский Д. В. — В сб.: «Катализ и методы изучения катализаторов». Алма-Ата, «Наука», 1967, стр. 131.

233. Schwarzenbeck E. T. Катализаторы из платины и палладия. Пат. США 276 0940, 28.08.56.

234. Миначев Х. М., Шуйкин Н. И., Ряшенцева М. А., Кононов Н. Ф. — «Изв. АН СССР, отд. хим. наук», 1958, № 6, 719.

235. Шуйкин Н. И., Миначев Х. М., Ряшенцева М. А. — «Докл. АН СССР», 1955, 101, № 1, 107.

236. Миначев Х. М., Ряшенцева М. А., Рубинштейн А. М. — «Изв. АН СССР, отд. хим. наук», 1959, № 5, 819.

237. Го Сы-сянь, Се Ань-хуэй и Гуо Чжун-жу. — В сб.: «Проблемы кинетики и катализа». М., Изд-во АН СССР, 1960, X, стр. 435.

238. Ряшенцева М. А., Афанасьева Ю. А., Миначев Х. М. — «Нефтехимия», 1963, 3, № 1, 55.

239. Houdry E. H. Катализ. Труды Первого международного конгресса. М., ИЛ., 1960, 562.

240. Эди В., Кольверт В. Катализ. Труды Первого международного конгресса. М., ИЛ, 1960, 861.

241. Эди В., Кольверт В. — «Химия и химическая технология», 1957, № 11, 193.

242. Lefrancois Ph. A., Riblett E. W., Burton W. P. Платиновый или палладиевый катализатор с применением соединения металлов группы III. Пат. США № 2814599, 26.11 1957.

243. Котелков Н. З. — «Ж. анал. хим.», 1950, 5, вып. 1, 48; «Ж. прикл. хим.», 1951, 24, 205.

244. Гершенович М. С., Котелков Н. З. — «Ж. прикл. хим.», 1954, 27, 1231; «Ж. прикл. хим.», 1938, 11, № 2, 253.

245. Баландин А. А., Котелков Н. З. — «Ж. прикл. хим.», 1942, 15, № 3, стр. 139.

246. Котелков Н. З. — Труды Саратовского с.-х. ин-та, 1966, 1(12), 272; «Ж. прикл. хим.», 1957, 30, 470.

247. Marcell Sam Anthony. Некорродирующий флюс и метод его приготовления. Пат. США, 3003901. 10.10.61.

248. Павлова В. Г., Шаповалов А. И., Либерова Р. А., Жуманов С. Л., Гордон О. Н. Способ нанесения рисунков на керамические и стеклянные изделия. Авт. св-во СССР, 147518 от 21.05.62.

249. Процесс металлизации керамики и керамических изделий, изготовленных по этому процессу. Франц. пат. CO4b, № 1335707, 15.07.63.

250. Казначей Б. Я. Гальванопластика в промышленности. М., Гос. изд-во мест. пром. РСФСР, 1955, стр. 65, 165.

251. Евтеев Ф. Е., Жуков В. А. Технология радиоаппаратуры. Л. — М., Госэнергоиздат, 1952, 84.

252. Захарьевский М. С. — «Зав. лаб.», 1940, № 5—6, 647.

253. Рабинович В. А., Куровская О. В. — «Почвоведение», 1953, № 4, 78.

254. Tlague E. D. Производство катализаторов из металла платиновой группы. Англ. пат. 832031, 6.04.60.

255. «Ceramics», 1960, 2, № 132, 14.

256. Houdry E. H. and Hayes C. T. — «Platinum Metals Review», 1, 1958, 2, № 4, 110.

257. Houdry E. H. Катализатор окисления. Швейц. пат. № 322973, 31.08.57.

258. Lacroix Roger. Приготовление Ag-катализаторов. Фр. пат. 1259574, 20.03.61.

259. Ямпольский Я. М. Гальванотехника драгоценных и редких металлов. М. — Л., Машгиз, 1958, 35.

260. Каданер Л. И. Защитные пленки на металлах. Харьков, Изд. Харьк. ун-та, 1956, 241.

261. Гинберг А. М. Гальванопластическое изготовление точных полых деталей. Л., Судпромгиз, 1949, стр. 20, 23, 27.

262. Мельникова Н. В., Сизов С. Н. Электролитические покрытия алюминия и его сплавов. М., ЦБТИ, 1958, 2.

263. Ternision J. A. «Metaux. Corrosion-Industries», 1959, № 409—412, 325.

264. Ивановский Ф. П., Семенова и др. — В сб.: «Химия и технология азотных удобрений. Очистка газа». М., 1965, стр. 24.

265. Ганз С. Н., Кузнецов И. Е. — Тезисы конференции по методам очистки газовых выбросов и пром. стоков от вредных веществ. Дзержинск, 1967, стр. 171.

266. Сокольский Д. В., Попова Н. М., Сыздыкбаева М. Б. Способ обезвреживания газов, содержащих окись углерода. Авт. св-во СССР, 166656, 01.12. 1964, бюллетень № 23, 12g, 3 01.

267. Сокольский Д. В., Попова Н. М., Сыздыкбаева М. Б., Алексеева Г. К. Способ очистки кислородсодержащих газовых смесей от окиси углерода. Авт. св-во СССР, 217389, 07.5. 1968, бюллетень № 16, 12q, 3/01.

268. Тюрин Ю. М., Феоктистов Л. Г. — «Кинетика и катализ», 1963, 4, вып. 2, 2[illegible]

269. Лопаткин А [illegible]. Стрельникова Ж. В., Лебедев В. П. — «Ж. физ. хим.», 1957, 31, вып. 8, 1820.

270. Стрельникова Ж. В., Лопаткин А. А., Лебедев В. П. — «Ж. физ. хим.», 1956, 30, вып. 3, 639.

271. Стрельникова Ж. В., Лопаткин А. А., Лебедев В. П. — «Ж. физ. хим.», 1956, 30, вып. 1, 196.

272. Лопаткин А. А., Стрельникова Ж. В., Лебедев В. П. — «Вестник Моск. гос. ун-та, сер. хим.», 1956, № 1, 255.

273. Рогинский С. З. Адсорбция и катализ на неоднородных поверхностях. М. — Л., Изд-во АН СССР, 1948, стр. 359, 533.

274. Крылов О. В., Рогинский С. З. — «Докл. АН СССР», 1953, 88, № 2, 293.

275. Крылов О. В., Рогинский С. З., Третьяков И. И. — «Докл. АН СССР», 1953, 92, № 1, 75.

276. Шехтер А. Б., Третьяков И. И. — «Изв. АН СССР, отд. хим. наук», 1953, № 3, 443.

277. Елович С. Ю., Розинг В. С. — «Проблемы кинетики и катализа», 1940, 4, 206; Рогинский С. З., Розинг В. С. — «Ученые зап-ки ЛГУ, сер. физ. наук», 1939, вып. 5, № 38, 67.

278. Рогинский С. З., Третьяков И. И., Шехтер А. Б. — «Ж. физ. хим.», 1949, 23, вып. 1, 50.

279. Рубинштейн А. М., Миначев Х. М., Шуйкин Н. И.— «Докл. АН СССР», 1950, 71, № 6, 1073.

280. Рубинштейн А. М., Миначев Х. М., Акимов В. М. — «Ж. общ. хим.», 1959, 29, вып. 8, 2503.

281. Маслянский Г. Н. Камушер Г. Д., Мушенко В. М. Способ приготовления платинового катализатора. Авт. св-во СССР, № 108258, 17.11.66, 12g, 11/16.

282. Казакова Е. А., Хитерер Р. З., Линдин В. М., Бомштейн В. Е., Савостьянова Н. С., Мировская В. И., Гудзенчук Ю. А., Медведева В. П., Коникова С. В., Вайнштейн Р. З., Румянцева М. С. В сб.: «Химия и технология азотных удобрений. Очистка газа». М., 1965, стр. 47.

283. Вагнер П. Минеральное сырье и цветные металлы. М. — Л., Цветметиздат, 1929, стр. 11—12.

284. Ивашенцев Я. И., Тимонова Р. И. — «Ж. неорг. и общ. химии», 1959, 12, 592.

285. Stover W. A., Briggs W. S. Метод очистки выхлопных газов. Пат. США 3304150, kl. 23—2, 14.3.1967.

286. Каданер Л., Дик Г. — «Ж. прикл. хим.», 1962, 35, 1.

287. Пилите С. П., Витомирскис Р. М. и др. — Труды АН Литовской ССР, Б., № 1 (44), 1962, 25.

288. Гармонов Н. В., Клебанский А. Л., Чевычалова К. К. — «Ж. общ. хим.», 1959, 29, 3, 836.

289. Клевке В. А., Кантор Д. С., Серегина Р. П. Способ регенерации палладиевого катализатора. Авт. св-во СССР, № 202077. Бюллетень изобретений, 1967, № 19; Клевке В. А., Кантор А. С., Серегина Р. П. Способ регенерации металлов платиновой группы. Авт. св-во СССР, № 197522, 9.6.67, 12g, 11/8.

290. Conner H. — «Chem. Ind.», 1960, № 48, 1454.

291. Hermann B., Christa K., Werner N.— «Chem. Ind.», 1964, 16, № 7, 382.

292. Гинзбург С. И., Гладышевская К. А., Езерская Н. А. и др. Руководство по химическому анализу платиновых металлов и золота. М., «Наука», 1965.

293. Fresenins W., Jander V. Handbuch der analytische chem., 1951, 8, B4, 385, Berlin.

294. Andolf H. Способ выделения палладия из кислых растворов. Пат. ФРГ, № 120569, 1966; пат. США 3294483, kl. 23—87, 27.X 1966.

295. Николаева М. И., Шлыгин А. И. — «Ж. физ. хим.», 1956, 30, вып. 8, 1729.

296. Вишомирскис Р. М., Молчадский А. М. — Труды АН Литовской ССР Б., № 1 (44), 1968, 37.

297. Вишомирскис Р. М., Моргенштерн Я. Л. — Труды АН Литовской ССР, Б., № 1 (44), 1966, 46.

298. William M., Macnevin, Warren B., — «Analyt. chem.». 1953, 25, № 11, 1628.

299. Миначев Х. М., Шуйкин Н. Н. и др. — «Докл. АН СССР», 1954, 99, № 5, 1015.

300. Пшеницин Н. К., Гладышевская К. А., Рязова Л. М. — «Ж. неорг. хим.», 1957, 2, вып. 5, 1057.

301. Плаксин И. Н., Шабарин С. К. — «Ж. прикл. хим.», 19, 1949, № 7—8, стр. 1021.

302. Крафт М., Шпиндлер Г.— В сб.: «Четвертый международный конгресс по катализу». М., 1968, доклад 69.

303. Rienäcker G. Abhandlungen der Deutschen Akad. der Wissenschaften zu Berlin. Beitrage zur Kenntnis der Wirkungsweise von Katalysatoren und Mischkatalysatoren, 1956, 45.

304. Карнаухов А. П. — «Кинетика и катализ», 1962, 3, вып. 4, 583.

305. Боресков Г. К., Чесалова В. С. — «Хим. пром-сть», 1960, № 6, 38.

306. Сокольский Д. В., Гильдебранд Е. И. — «Докл. АН СССР», 1949, 133, № 3, 609.

307. Гильдебранд Е. И. — В сб.: «Катализаторы на носителях». Алма-Ата, «Наука», 1965, 107.

308. Скопин Ю. А. Изучение порошковых катализаторов электрохимическими методами. Автореферат диссертации. Алма-Ата, 1963.

309. Гильдебранд Е. И. Активность тонких слоев платины и палладия на носителях. Кандидатская диссертация. Алма-Ата, 1962.

310. Сокольский Д. В., Гильдебранд Е. И. — «Ж. физ. хим.», 1955, 29, 760.

311. Сокольский Д. В. — «Вестник АН КазССР», 1954, № 8, 66.

312. Сокольский Д. В.— В сб.: К юбилею республики, Казучпедгиз, 1961, 215.

313. Сокольский Д. В., Левченко Л. В. — «Вестн. АН КазССР», 1954, № 1, 92.

314. Сокольский Д. В., Попова Н. М. — «Вестн. АН КазССР», 1957, № 1.

315. Сокольский Д. В. — «Вестн. АН КазССР», вып. 4, 1968.

316. Гоголь Н. А. Каталитические свойства Pd на носителях при гидрировании непредельных спиртов. Автореферат диссертации. Алма-Ата, 1967.

317. Сокольский Д. В. — В сб.: «Четвертый международный конгресс по катализу». М., 1968, 45 доклад.

318. Конозенко И. Д. — «Успехи физ. наук», 1954, 52, № 4, 561.

319. Сельвуд П. У. Катализ. Вопросы теории и методы исследования, 1955, М., 391.

320. Кобозев Н. И., Евдокимов В. Б., Зубович И. А., Крылова И. В., Лебедев В. П., Мальцев А. Н., Некрасов Л. И., Поспелова Т. А. — «Ж. физ. хим.», 1959, 33, № 12, 2811.

321. Nikolau C., Thom H. — «Trans. Farad. Soc.», 1959, 55, 1430.

322. Бурсиан И. Р., Коган И. Р., Давыдова З. А. — «Кинетика и катализ», 1967, 8, вып. 6, 1283.

323. Демочка О. К. Пути уменьшения вредности отработавших газов карбюраторных двигателей. НИИН Автопром., сер. автомобилестроение. М., 1966.

324. **Nicolescu J. V., Popescu A. L.** — «Studii si cercetaride Chimie», 1959, 1, p. 49.

325. **Егоров М. М.** — «Докл. АН СССР», 1961, 140, № 2, стр. 401.

326. **Плясова Л. М., Кефели Л. М.** — «Кинетика и катализ», 1965, 6, № 6, 1080.

327. **Игнатова Л. А., Халикова Р. Х.** — «Ж. прикл. спектроскопии», 1966, 5, № 5, 642.

328. **Долидзе Г. М., Колбановский Ю. А., Полак Л. С.** — «Кинетика и катализ», 1965, 6, 897.

329. **Боресков Г. К., Дзисько В. А.** — «Ж. физ. хим.», 1952, 26, 492.

330. **Топчиева К. В., Московская И. Р.** — «Вестн. Моск. гос. ун-та», 1960, № 2, 22.

331. **Low M. J. D., Argano E. S.** — «J. Phys. Chem.», 1966, 70, № 10, 3115.

332. **Боресков Г. К., Дзисько В. А., Борисова М. С.** — «Ж. физ. хим.», 1953, 27, № 8, 1176.

333. **Рубинштейн А. М., Словецкая К. И., Бруева Т. Р., Федоровская Э. А.** — «Докл. АН СССР», 1966, 167, 1308.

334. **Сельвуд П. У.** — В сб.: «Четвертый международный конгресс по катализу». М., 1968, 66 доклад.

335. **Henrici-Olive F., Olive S.** — «Chimia», 1967, 21, № 2, 87.

336. **Левина С., Фрумкин А., Лунев А.** — «Ж. физ. хим.», 1936, 7, 664.

337. **Фрост А. В., Лапин Ю. П., Мальцев А. П., Кобозев Н. И.** — «Вестн. МГУ», 1946, № 1, 95.

338. **Шехобалова В. И., Крылова И. В., Кобозев Н. И.** — «Ж. физ. хим.», 1952, 26, № 5, 703.

339. **Мальцев А. Н., Кобозев Н. И.** — «Ж. физ. хим.», 1955, 29, вып. 2, 291, 142.

340. **Шехобалова В. И., Крылова И. В., Кобозев Н. И.** — «Ж. физ. хим.», 1952, 26, № 11, 1966.

341. **Стрельникова Ж. В., Лебедев В. П.** — «Вестн. МГУ», 1966, № 5, 11.

342. **Лебедев В. П.** Структурные валентные и кинетические характеристики активных центров адсорбционных смешанных и поликристаллических металлических катализаторов. Докт. дисс. М., 1964.

343. **Эйдус Я. М.** — «Изв. АН СССР, отд. хим. наук», 1953, № 6, 1025.

344. **Эйшенс Р., Плискин В.** Катализ. Исследование поверхности катализаторов. М., ИЛ., 1960, стр. 22.

345. **Сельвуд П., Бернелл Р., Эйшенс Р.** Новые методы изучения гетерогенного катализа. М., ИЛ, 1963, стр. 80.

346. **Rienäcker G.** — «Über Trägerkatalyse», Sitzungberichte Dtsch. Acad. Wiss. Zu Berlin, Kl. Geol. Biol., 1964, № 3.

347. **Бурсиан Н. Р., Волнухина Н. К.** — «Ж. прикл. хим.», 1966, № 4, 845.

348. **Миначев Х. М., Шуйкин Н. И., Виноградов В. А.** — «Изв. АН СССР, отд. хим. наук», 1958, № 7, 866; **Миначев Х. М., Шуйкин Н. И** — «Докл. АН СССР», 1954, 99, № 5, 1015; **Шуйкин Н. И., Миначев Х. М., Тулупова Е. Д., Егоров Ю. П.** — «Докл. АН СССР», 1954, 99, № 6, 1211.

349. **Хасин А. В., Боресков Г. К., Старостина Т. С.** — В сб.: «Методы исследования катализаторов и каталитических реакций», 1. Новосибирск, Изд. СО АН СССР, 1965, 342.

350. **Бортнер М. И., Парравано Г.** Катализ. Труды Первого международного конгресса. М., ИЛ, 1960, стр. 480.

351. **Миркин А. И.** Справочник по рентгеноструктурному анализу поликристаллов. М., Изд. физ-мат. лит., 1961.

352. **Spenadel B. G., Boudart M.** — «J. Phys. Chem.», 1960, 64, № 2, 204.

353. **Карнаухов А. П.** Методы исследования структуры высокодисперсных и пористых тел. М., Изд-во АН СССР, 1953, стр. 145.

354. **Шехтер А. Б., Ечеистова А. И., Третьяков И. И.** — «Докл. АН СССР», 1949, 68, № 6, 1069.

355. **Chu B. B.** — «Z. Phys. Chem.», 1963, 67, № 9, 1916.

356. **Грязнов В. М., Ягодовский В. Д., Шимулис В. И.** — «Кинетика и катализ», 1961, 2, вып. [illegible], 221.

357. **Николаев А. В.** — «Докл. АН СССР», 1938, 20, № 7—8, 577.

358. **Боресков Г. К.** — «Ж. физ. хим.», 1956, 30, вып. 3, 704.

359. **Крылов О. В., Рогинский С. З.** — «Изв. АН СССР, отд. хим. наук», 1956, № 2, 145.

360. **Крылов О. В., Рогинский С. З., Третьяков И. И.** — «Докл. АН СССР», 1953, 91, № 6, 1353.

361. **Давтян О. К.** — «Ж. физ. хим.», 1964, 38, вып. 5, 1077.

362. **Ария С. М., Морозова М. П., Рейхард А. А.** — «Ж. общ. хим.», 1953, 23, № 9, 1455.

363. **Briggs W. S., Stover W. A., Warthen J. L.** Метод очистки выхлопных газов. Пат. США 3295918, kl. 23—2, 3. 1. 1967.

364. **Марголис Л. Л., Тодес О. М.** — «Докл. АН СССР», 1946, № 6, 519.

365. **Kazuo Mitani, Joshio Harauo.** — «Bull. Chem. Soc. Japan», 1960, 33, № 2, 276.

366. **Ададуров И. Е., Диденко П. Д.** — «Ж. прикл. хим.», 1935, № 5, 823.

367. **Рогинский С. З.** Проблемы кинетики и катализа, 1940, 4 187.

368. **Крылов О. В., Рогинский С. З., Третьяков И. И.** — «Докл. АН СССР», 1953, 91, № 6, 1353.

369. **Добычин Д. П., Клибанова Ц. М.** Алюмосиликатные катализаторы. М., Гостоптехиздат, 1952, 318.

370. **Боресков Г. К., Дзисько В. А., Борскова М. С., Краснопольская В. Н.** -- «Ж. физ. хим.», 1952, 26, вып. 4.

371. **Красильников К. Г., Киселев В. Ф., Капитанова Н. В., Сысоев Е. А.** — «Ж. физ. хим.», 1957, 31, вып. 7, 1448.

372. **Красильников К. Г., Киселев В. Ф.** — «Проблемы кинетики и катализа», 1960, 10, 421.

373. **Масагутов Р. М., Галимов Ж. Ф., Дубинина Г. Г., Морозов Б. Ф.** — В сб.: «Методы исследования катализаторов и каталитических реакций», 2. Новосибирск, Изд. СО АН СССР, 1965, 202. 202.

374. **Киселев А. В., Леонтьев Е. А., Лукьянович В. М., Никитин Ю. С.** — «Ж. физ. хим.», 1956, 30, вып. 10, 2149.

375. **Морозов Б. Ф., Масагутов Р. М., Дубинина Г. Г.** — В сб.: «Методы исследования катализаторов и каталитических реакций», 2. Новосибирск, Изд. СО АН СССР, 1965, 284.

376. **Афанасьев В. А.** — Автореферат диссертации. М., Ин-т орг. химии АН СССР, 1955.

377. **Рубинштейн А. М., Афанасьев В. А.** Прибор для определения удельной поверхности катализаторов в проточной системе при атмосферном давлении. Передовой научно-произв. опыт. М., Ин-т научн. инф. 1957.

378. **Рубинштейн А. М., Афанасьев В. А.** — «Изв. АН СССР, отд. хим. наук», 1956, вып. 11, 1294.

379. Клячко-Гурвич А. Я. — «Изв. АН СССР, отд. хим. наук», 1961, № 6, 1884.

380. Буянова Н. Е., Гудкова Г. Б., Карнаухов А. П. — В сб.: «Методы исследования катализаторов и каталитических реакций», 2. Новосибирск, Изд. СО АН СССР, 1965, стр. 55; Карнаухов А. П.— Там же, стр. 95.

381. Donald G. M., Fred J., Kice Jr. — «J. Phys. Chem.», 1961, 68, № 2, 420.

382. Kral H. — «Z. Physik. Chem.», N. F., 1966, 48, № 3—4, 129; 1966, 48, № 3—4, 129.

383. Dorling T. A.,Moss R. L. — «J. Catalysis», 1967, 7, № 4, 378.

384. Sugita T., Ebisama T., Kawasaki K. — «Surtace Science», 1968, 11, № 1, 159.

385. Новиков С. С., Рубинштейн А. М., Шуйкин Н. И.— «Докл. АН СССР», 1948, 62, № 3, 345.

386. Емельянова Г. И., Хасан С. — В сб.: «Четвертый международный конгресс по катализу». М., 1968, 73 доклад.

387. Р. ван Харделд, Хартог Ф. — В сб.: «Четвертый международный конгресс по катализу». М., 1968, 70 доклад.

388. Sinfelt J., Hurwitz H., Rohres J.— «J. Phys. Chem.», 1960, 64, № 7, 892.

389. Иванов К., Кобозев Н. — «Ж. физ. хим.», 1937, 10, вып. 1, 1.

390. Бессалов П., Кобозев Н. — «Ж. физ. хим.», 1937, 9, вып. 6.

391. Шехтер А. Б., Ечеистова А. И., Третьяков И. И. — «Изв. АН СССР, отд. хим. наук», 1951, № 1, 42.

392. Ерофеев Б. В. Переходные металлы и их каталитические свойства. М., «Знание», 1966.

393. Ерофеев Б. В., Иванькевич Е. Ф., Никифорова Н. В. — «Проблемы кинетики и катализа», 1966, 11, стр. 86.

394. Корш М. Г., Мартынова В. М. — «Хим. пром-сть», 1959, № 7, 37.

395. Алексеева Г. К. — Кандидатская диссертация. Алма-Ата, 1968.

396. Алексеева Г. К., Ольшанская Н. И. — Труды Ин-та хим. наук АН КазССР. Алма-Ата, 1969, 26, стр. 129.

397. John Hubert Beck, Alvin Barber Stiles. Получение катализаторов на носителях. Пат. США, 3161605, 15.12.64, kl. 252—455.

398. Jerome W. Приготовление катализаторов Pt-группы. Пат. США 2802794, kl. 252—466, 21.12.53.

399. Howard M. Составы для покрытия палладием. Пат. США 3216834, kl. 106—1, 5.10.60.

400. Бурсин Н. Р., Коган С. Б., Давыдова З. А. Способ получения Pt-катализатора. Авт. св-во СССР, 182119, 5.1.66.

401. Бурсиан И. Р., Коган С. Б., Осмоловский Г. М., Людковская Б. Г., Давыдова З. А. — В сб.: «Методы исследования катализаторов и каталитических реакций». Новосибирск, СО АН СССР, 1965, 2, стр. 144.

402. Benninghoff Hanns — «Galvanotechnik», 1966, 57, № 12, 853; 1967, 58, № 1, 14.

403. Huber Willy — «Techn. Rundschau», 1965, 57, № 31, 39.

404. Reid F. H. — «Metallurg. Rev.», 1963, 8, № 30, 167.

405. Бахвалов Г. М., Лайнер В. И., Масленникова А. С. -- «Изв. вузов, цветная металлургия», 1966, № 1, 148.

406. Марков М. И., Харламова К. Н., Кудрявцева Л. В.—

Труды Всесоюзного научно-исслед. и конструкторского ин-та хим. машиностроения, 1966, вып. 51, 136.

407. Brace A. W. — «Industr. Finish» (Engl.), 1965, 17, № 209, 34.

408. Антошин Г. В., Миначев Х. М., Дмитриев Р. В. — «Изв. АН СССР, сер. хим. наук»., 1967, № 8, 1864.

409. Ochs Hans-Joachim. — «Wasser, Luft und Betrieb», 1966, 10, № 2, 71.

410. Bernert Jungen. — «Wasser, Luft und Betrieb», 1965, 9, № 4, 215, 235.

411. Betz S. C., Feist H. J. — «Technik», 1965, 20, № 6, 395.

412. Голубев В. Б., Евреинов В. И. — «Ж. физ. хим.», 1966, 40, 2841.

413. Дзисько В. Д., Кефели Л. М., Винникова Ж. С., Рыжак И. Л. — «Кинетика и катализ», 7, вып. 5, 1966, 859.

414. Авдеенко М. А., Боресков Г. К., Слинько М. Г. — «Проблемы кинетики и катализа», 1957, 9, стр. 61; Боресков Г. К.— «Ж. физ. хим.», 1957, 31, 937.

415. Carter J. L., Luechesit P. J., Sinfelt J. H., Jates D. J. C. Prepr. Poc. 3-rd Inbernat. Congress. Catalysis, 1964, № 1137, 10.

416. Сокольский Д. В., Жусупбеков Б. О. — «Докл. АН СССР», 170, 1966, 1096; Сокольский Д. В., Жусупбеков Б. О.— «Кинетика и катализ», 1968, 9, 194.

417. Шашков А. С., Мозжихина А. С., Крылова И. В., Кобозев Н. И. — «Ж. физ. хим.», 1960, 40, № 8, 1965.

418. Шехобалова В. И., Кобозев Н. И. — «Ж. физ. хим.», 1963, 37, № 9, 2131.

419. Фрумкин А. Н. Катализ. Труды третьей конференции по физико-химии катализа. Л., 1930, вып. 26, стр. 54.

420. Сокольский Д. В., Жусупбеков Б. О. — «Ж. физ. хим.», 1967, 41, 1213.

321. Кавтарадзе Н. Н., Соколова Н. П. — В сб.: «Методы исследования катализаторов и каталитических реакций». Новосибирск, Изд. СО АН СССР, 1965, 1, 109, 95; «Ж. физ. хим.», 1962, 36, 2804.

422. Adler S. F., Keavney J. J. — «J. Phys. Chem.» 1960, 64, № 2, 208.

423. Миначев Х. М., Шуйкин Н. И., Виноградов В. Л. — «Изв. АН СССР, отд. хим. наук», 1958, № 7, 866.

424. Митрофанова А. Н., Боронин В. С., Полторак О. М. — «Вестн. МГУ», 1966, № 5, 40.

425. Лопаткин А. А., Стрельникова Ж. В., Лебедев В. П. — «Ж. физ. хим.», 1957, 31, № 8, 1820.

426. Maxted E. B., Sajeed Akhtar. — «J. Chem. Soc.», 1960, № 6, 1995; Maxted E. B., Ismail S. M. — «J. Chem. Soc.», 1962, № 6, 2330; Maxted E. B., Ali S. J. — «J. Chem. Soc.», 1961, № 9, 4137.

427. Бонд Дж. К. — В сб.: «Четвертый международный конгресс по катализу». М., 1968, 67. Доклад.

428. Flochart B. D., Scott J. A., Pink R. C. — «Trans. Far. Soc.», 1966, 62, 730.

429. Баранчевский В. А., Холмогоров В. Е., Белоцерковский Г. М., Теренин А. Н. — «Кинетика и катализ», 1965, 6, 258.

430. Каракчиев Л. Г., Баранчевский В. А., Холмогоров В. Е. — «Кинетика и катализ», 1964, 5, 630.

431. Какабадзе В. М., Какабадзе И. Л.— Труды Груз. политехн. ин-та, 1957, № 54, стр. 66—76.

432. Пурцеладзе Х. Г., Джикия С. И., Курумидзе З. А.,

Чкония Т. К. — Труды Ин-та металла и горного дела АН Груз ССР, 1956, 7, 239.

433. Cohn G. E. Удаление окислов азота из газов. Пат. США 3118727, kl. 23—2, 21.12.1964.

434. Andersen H. C., Green W. J. Метод очистки газов, содержащих кислород, от окислов азота. Пат. США 2970034, kl. 23—2, январь 1961.

435. Andersen H. C. Очистка газов, содержащих O_2 и окислы азота. Пат. США 3053613 kl. 23—2, 11.09.62.

436. Childers E., Ellis Ch. W., James R. D. Метод удаления окислов азота из газов. Пат. США 3125408 kl. 23—2, 17.03.64.

437. Andersen H. C., Keith C. D. Метод очистки газов, содержащих кислород, от окислов азота. Пат. США 3008796, kl. 23—2, 15.6.62.

438. Фурманов А. С., Клевке В. А., Язбель И. Я., Горфункель В. Е.— «Хим. пром.», 1968, № 7, 520.

439. Fraser J. M., Daniels F. — «J. Phys. Chem.», 1958, 62, № 2, стр. 215.

440. Ивановский Ф. П., Семенова Т. А., Миркина М. И., Штейнберг Б. И. Способ приготовления катализатора для очистки конвертированного газа от окислов азота, ацетилена, кислорода на основе солей палладия и рутения. Авт. св-во СССР, 165675, 26.10. 1964.

441. Roth J. F., Doer R. C. — «Ind. Eng. Chem.», 1961, № 4, 53.

442. Catalytic Combustion Corporation. Brit. pat. 775549; 775550; Du Pont de Nemours, Brit. pat., 799159, 6.8. 1958.

443. Fletcher W. «British chem. Eng.», 1960, 5, № 11, 789.

444. Aven R. J., Peters M. S. — «Ind. eng. Chem. Proc. Design. Development», 1962, 1, № 3, стр. 204.

445. Wikstrom L. L., Nobe K. — «Ind. Eng. Chem. Process Design and Development», 1965, 4, № 2, 191.

446. Baker R. A., Doer R. C. — «Ind. Eng. Chem. Process Design and Development», 1965, 4, № 2, 188.

447. Sakaida R. R., Rinker R. G., Wang I. L., Corcaran W. H., A. Inst. Chem. E. Journal, 1961, № 12, 658.

448. Школьман Е. Е. Губергриц М. Я. — «Ж. хим. пром.», 1941, № 3, 6.

449. Шполянский М. А., Бережнов Б. И., Грузинцева А. И. — «Хим. пром-сть», 1950, № 4, 101.

450. Науффе К., Шлоссер Э. — Труды Первого международного конгресса по катализу. М., ИЛ, 1960, стр. 108.

451. Cronan C. S. — «Chem. Eng.», 1959, 66, № 1, 66.

452. Benton A. F., Thacker C. M. — «J. Am. Chem. Soc.», 1934, 56, № 6, 1300.

453. Тупяков О. Д. — В кн.: «Производство аммиака и азотной кислоты». Ин-т н.-техн. информ. и науч. пропаганды УзбССР, Ташкент, 1965, стр. 270.

454. Калугина Т. Д. — Там же, стр. 275.

455. Ганз С. Н. — «Ж. прикл. хим.», 31, 1958, вып. 1, 139; 31, 1958, вып. 3, 367.

456. Царев В. В., Гавшин А. Л. — В сб.: «Токсичность двигателей внутреннего сгорания». М., «Наука», 1966, стр. 399.

457. Юрьева Т. М., Поповский В. В., Боресков Г. К. — «Кинетика и катализ», 6, 1965, вып. 6, 1041.

458. Kokes R. J. — «J. Phys. Chem.», 1966, 70, 296.

459. Vance J. E., Dixon J. K. — «J. Am. Chem. Soc.», 1941, 63, № 1, 176.

460. Shelef M., Otto K. — «J. Catalysis», 1968, 10, № 4, 408.

461. Ивановский Ф., Корш М., Криштул Е. — «Ж. хим. пром-сть», 1935, № 8, 803.

462. Миннович М. А. — «Ж. прикл. хим., 1958, 31, вып. 8, 1129.

463. Чернышев А. К., Занчко Н. Д. — «Хим. пром-сть за рубежом». М., НИИТЭХИМ, 1966, № 1, 20.

464. Andersen H. C., Green W. J., Steele D. R. — «Ind. Engng. Chem.», 1961, 53, № 3, 199; Andersen H. C., Cohn G., en W. J., Steele D. R., Франц. пат. 1205311, 2. III. 1960; Andersen H. C., Keith C. D. — Франц. пат. 1233712, 9. V 1960.

465. Chilton C. H. «Chem. Engng.», 1958, 15, № 18, 58.

466. «Chem. Engng.», 1961, 68, № 21, 102.

467. Fraser D. S. C. — «British. Chem. Engng.», 1962, № 3, 50.

468. Drake G. — «British Chem. Engng.», 1963, 8, № 1, 12.

469. «Chem. Eng. News.», 1956, 34, № 34, 4096.

470. Matrien-Zevy L. S. — «Annales des Mines», 1949, 138, № 3, 23.

471. Миначев Х. М., Кондратьев Д. А., Антошин Г. В. — «Кинетика и катализ», 1967, 8, № 1, 131.

472. Kainz G., Horwatitsch H. — «Mikrochimica Acta», 1962, 1, № 1—2, стр. 7.

473. Sourirayan S., Blumenthal J. L.— Actes du Deuxieme Kongrés Internat. de Catalyse, Paris, 1960. Copyright Editions Technik., 2, 2521.

474. Michailova E. A. — «Acta Physikochimica URSS», 1939, 10, № 5, 653.

475. Sourirayan S., Blumenthal J. L. — «Air and Water Pollution an Internat. Journal», 1961, 5, № 1, 24.

476. Duparc L., Wenger P., Urfer Ch. — «Helvetica chimica Acta», 1925, 8, вып. 609.

477. Schwab G. M., Drikos G. L. — «Phys. Chem., Abt. A.», 1940, № 6, 348.

478. Eugene Childers, Charles Welliam Ellis, Donald James — Пат. США 2910343, kl. 23—2, 27.10 1959.

479. Noimenmacher H., Kartte K. Селективная очистка смесей, содержащих O_2, от окислов азота. Пат. США 3279884, kl. 23—2, 18.10. 1966.

480. Keith C. D., Kenah P. M. Процесс каталитической очистки газов, содержащих окислы азота. Пат. США 3328115, kl. 23—2.

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